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ATMOSPHERIC OZONE

A survey of the current state of knowledge of the ozone layer, including mechanisms which may change ozone amounts, possible climatic consequences of such changes, and recommendations for further monitoring and research.

Submitted by

THE WORLD METEOROLOGICAL ORGANIZATION

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Note

Readers for whom a summarized form of this document is sufficient may confine their attention to Sections I, V and VI.

I. INTRODUCTION

The Problem

1. In recent years there has been increasing concern as to the effects of the pollution of the stratosphere, and in particular the possibility of a reduction in the amount of ozone present at these levels due to photochemical reactions involving certain trace substances, the concentration of which may be increased due to human activities. This concern arises from the danger of increased solar ultraviolet radiation penetrating to the Earth's surface and from the possibility of induced changes in the global climate.

Some of WMO's activities in connexion with atmospheric ozone

2. WMO was first involved in this field by collecting and publishing world ozone data for the International Geophysical Year (IGY) and International Geophysical Co-operation (IGC). Following a decision by the Third World Meteorological Congress in 1959 to extend WMO's sphere of action to include responsibilities in international ozone work, Members were urged to establish total ozone observing stations and programmes of ozonesondes to measure the vertical ozone distribution. WMO regional associations were asked to designate at least one of their ozone stations as a regional standard.

3. Following the IGY, WMO has sponsored, by arrangement with the Atmospheric Environment Service of Canada, the continued publication of world ozone data. These were issued annually for the years 1960 to 1964, and since 1965 the data have been published bi-monthly in order to get them to research workers more quickly. A catalogue containing a list of stations measuring atmospheric ozone and giving the programme of observations was first published in 1962 and is continuously updated and incorporated periodically in the bulletins issued by the World Ozone Data Centre at Toronto.

4. In response to increasing public concern as to the possibility of a depletion of the stratospheric ozone due to pollutants resulting from human activities, and the attendant risk of increased amounts of solar ultra-violet radiation reaching the Earth's surface, some nationally sponsored studies of the problem have been undertaken, notably the Climate Impact Assessment Program (CIAP) of the U.S.A.

5. The Seventh World Meteorological Congress (May, 1975) agreed that "there was an urgent need for more studies (and for a definitive review of these studies) to determine the extent to which man-made pollutants might be responsible for reducing the quantity of ozone in the stratosphere". Additionally, Congress "stressed the need to determine the role played by chlorofluoromethanes (used in refrigerants and aerosol cans) in destroying ozone. As part of these studies, the global ozone-monitoring system should be strengthened and in this connexion the Secretary-General was requested to examine the possibility of collaborating with UNEP within the context of its Global Environment Monitoring System (GEMS)"*.

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* Abridged report of Seventh Congress, general summary paragraph 3.2.1.3

6. Some four months later, the ICSU International Union of Geodesy and Geophysics (IUGG) at its sixteenth General Assembly in Grenoble (France) in turn called for greater efforts in research to increase our knowledge of processes affecting the upper atmosphere, with special emphasis on the stratosphere and possible consequences of pollution therein, and urged co-operation in international monitoring and other activities aimed at determining any long-term trends in the stratosphere in so far as these might affect environmental quality. IUGG recommended that appropriate intergovernmental organizations, especially WMO, provide encouragement, support and co-ordination to such endeavours.

7. At a meeting in September 1975 the WMO Commission for Atmospheric Sciences Working Group on Stratospheric and Mesospheric Problems, together with some of the world's most eminent scientists in the field, discussed the subject of stratospheric ozone. Representatives of UNEP and ICSU took part in the meeting during which an official WMO statement entitled "Modification of the ozone layer due to human activities and some possible geophysical consequences" was drafted and subsequently released with the agreement of the WMO Executive Committee at the end of 1975. It was at this session also that the outline of a Global Ozone Research and Monitoring Project was formulated, further detailed elaboration being undertaken by a smaller ad hoc group of experts in January 1976 (with UNEP and ICSU again being represented).

WMO Global Ozone Research and Monitoring Project

8. At its twenty-eighth session in June 1976, the WMO Executive Committee adopted Resolution 8 (EC-XXVIII) and thereby approved the proposed Global Ozone Research and Monitoring Project. The resolution is reproduced in full in Appendix A.

9. The aim of the Project is to enable WMO to provide advice to Members and to the United Nations and other appropriate international organizations concerning:

(a) The extent to which man-made pollutants might be responsible for reducing the quantity of ozone in the stratosphere, with particular emphasis on the role played by chlorofluoromethanes and nitrogen oxides;

(b) The possible impact of changes in the stratospheric content of ozone on climatic trends and on solar ultra-violet radiation at the Earth's surface;

(c) The establishment of the basis and identification of the needs for strengthening the long-term monitoring programme of the ozone system for determination of trends and of future threats to the ozone shield.

10. The means by which the objectives may be achieved are as follows:

(a) To gather and evaluate existing knowledge on atmospheric ozone;

(b) To provide information on the atmospheric concentrations of substances of relevance to the N_2O, NO_x, HO_x, ClO_x, BrO_x cycles leading to a better appreciation of their currently-known important sources and sinks and their impact on the ozone budget;

(c) To extend and improve analyses and circulation studies of the stratosphere based on actual data, with a view to clarifying and predicting the exchange processes between the troposphere and the stratosphere;

(d) To assess the impact on the atmospheric environment of possible ozone depletion, recognizing that this involves a variety of interdisciplinary interactions requiring input from the fields of meteorology, oceanography, agriculture and microbiology;

(e) To arrange for an exchange of knowledge through reports, newsletters, scientific meetings and exchange of personnel.

11. The Global Ozone Research and Monitoring Project was welcomed by the International Ozone Commission of ICSU's International Association of Meteorology and Atmospheric Physics (IAMAP) which went on to recommend that all measures be taken to implement the proposals as completely and as quickly as possible, especially the monitoring of trace gases at ozone measuring stations.

A brief review of scientific progress

12. Ozone is formed at stratospheric levels as a result of the photodissociation of molecular oxygen. It is of major importance in the meteorology of the stratosphere, since by virtue of its absorption of solar ultra-violet radiation and the resulting heating effect, it largely determines the basic temperature structure and general circulation of this region. Moreover, since it behaves essentially as an inert tracer in the lower stratosphere, observations of its distribution provide considerable information on transport mechanisms in this region and also transfer between the stratosphere and troposphere.

13. If the ozone formation and destruction processes were determined solely by the photochemical reactions involving only the oxygen species (the Chapman reactions) no effects resulting from human activities would be expected. However, improved observations of the vertical distribution of ozone obtained during and after the International Geophysical Year made it clear that the pure oxygen photochemistry did not completely explain the actual processes found to be taking place, and subsequently the importance of stratospheric trace gases was discovered, especially the oxides of nitrogen (NO_x), in controlling the ozone balance. This led to the conclusion that ozone might be less stable against outside man-made influences than had previously been believed.

14. The main natural source of NO_x in the stratosphere is thought to be the oxidation of nitrous oxide (N_2O) (of biological origin at the surface of the Earth and the sea) by excited oxygen atoms which themselves are a product of the photodissociation of ozone. Other natural sources of NO_x whose magnitude is not yet well enough established are cosmic rays and solar proton events and downward transport from the thermosphere in high latitudes of the winter hemisphere. The possibility of some direct supply of NO_x from the troposphere below cannot be ruled out.

TABLE 1

ESTIMATE OF THE GLOBAL PRODUCTION OF CHLOROFLUOROMETHANES $CFCl_3$ & CF_2Cl_2

(in millions of pounds)

$CFCl_3$		YEAR	CF_2Cl_2	
Annual	Cumulative		Annual	Cumulative
.0	.0	1931	1.2	1.2
.0	.0	1932	.3	1.5
.0	.0	1933	.7	2.2
.1	.1	1934	1.5	3.7
.1	.2	1935	2.2	5.9
.2	.4	1936	3.8	9.7
.3	.7	1937	6.8	16.5
.2	.9	1938	6.2	22.7
.2	1.1	1939	8.7	31.4
.4	1.5	1940	10.0	41.4
.6	2.1	1941	13.8	55.2
.7	2.8	1942	13.1	68.3
.9	3.7	1943	18.1	86.4
.8	4.5	1944	36.9	123.3
.8	5.3	1945	44.3	167.6
1.6	6.9	1946	36.7	204.3
2.9	9.8	1947	44.4	248.7
6.6	16.4	1948	54.6	303.3
9.9	26.3	1949	57.6	360.9
14.6	40.9	1950	76.2	437.1
20.0	60.9	1951	79.9	517.0
29.9	90.8	1952	82.1	599.1
38.1	128.9	1953	102.5	701.6
46.1	175.0	1954	108.3	809.9
58.0	233.0	1955	128.0	937.9
71.7	304.7	1956	151.9	1089.8
74.9	379.6	1957	164.2	1254.0
65.4	445.0	1958	162.8	1416.8
78.8	523.8	1959	194.6	1611.4
110.1	633.9	1960	221.4	1832.8
133.8	767.7	1961	242.4	2075.2
173.2	940.9	1962	287.4	2362.6
207.2	1148.1	1963	329.8	2692.4
246.4	1394.5	1964	385.0	3077.4
273.8	1668.3	1965	432.0	3509.4
312.2	1980.5	1966	499.6	4009.0
359.9	2340.4	1967	567.2	4576.2
411.7	2752.1	1968	609.7	5185.9
491.0	3243.1	1969	685.4	5871.3
541.0	3784.1	1970	737.9	6609.2
604.2	4388.3	1971	783.0	7392.2
698.4	5086.7	1972	877.0	8269.2
809.1	5895.8	1973	970.2	9239.4
880.5	6776.3	1974	1041.9	10281.3
786.0	7562.3	1975	915.9	11197.2

Data from the Manufacturing Chemists' Association
1 March 1976

15. A theory has recently been propounded that increased use of agricultural fertilizers and/or of nitrogen-fixing vegetation might affect the nitrogen cycle and result in an increase in the amounts of nitrous oxide (N_2O) released from the surface into the atmosphere. This would then lead to an increase in NO_x in the stratosphere and hence a decrease in the ozone amount. This source of N_2O might also be stimulated by increases in the acidity of rain.

16. There has already been considerable research conducted into the direct injection of NO_x into the stratosphere by fleets of supersonic aircraft and the consequent effect on the ozone layer. Although there are considerable uncertainties in both measurements and theory (in the latter case being of about a factor of two), the role of NO_x is sufficiently well established to be able to state with reasonable confidence that:

- currently planned SSTs, due to their lower flight altitudes of 17 km and their limited numbers (fewer than 50 projected) are not predicted to have an effect that would be significant or that could be distinguished from natural variations;

- a large fleet of supersonic aircraft flying at greater altitudes is predicted to have a noticeable effect on the ozone layer, and permissible total emission levels may have to be defined by international agreement.

17. Recently it has been shown that ozone is also destroyed by the catalytic cycle of oxides of chlorine ($Cl\text{-}ClO_x$). In this case, ozone destruction is accelerated by increased HO_x, but retarded by the presence of methane and nitric oxide. The amount of naturally produced ClO_x in the stratosphere seems to be small and its effect on ozone considerably smaller than that of NO_x. The role played by the bromine $Br\text{-}BrO_x$ cycle could be similar to that of the $Cl\text{-}ClO_x$; but given equal amounts of Br and Cl in the stratosphere the former would be the most effective in destroying ozone.

18. The increase in the manufacture and release into the atmosphere of chlorofluoromethanes, especially $CFCl_3$ (F-11) and CF_2Cl_2 (F-12), see Table 1, is predicted to result in a rapidly increasing amount of ClO_x in the stratosphere. The removal rate of ClO_x is slow, it is to be expected that the stratospheric ClO_x concentration will continue to increase for several years even were all emissions of chlorofluoromethanes into the atmosphere to cease, due to the slow diffusion rates into and through the stratosphere. Thereafter the recovery rate would be very slow (a few decades).

Methods of measuring atmospheric ozone

19. At this point it may be useful to summarize briefly the kinds of measurements which are currently made of atmospheric ozone.

Total ozone (surface-based)

20. The total amount of ozone in the column of the atmosphere above the observing station is measured by a spectrophotometer. The instrument most generally

used is the Dobson ozone spectrophotometer which, although bulky and delicate, gives estimates of total ozone to within 2% if carefully operated and maintained. Certain other recently-developed spectrophotometers are being tested against the Dobson instrument with satisfactory results. WMO has periodically organized intercomparisons of Dobson ozone spectrophotometers, the latest having been at Aspendale (Australia) in 1972 and at Belsk (Poland) in 1974. The next is planned for the summer of 1977 in Boulder (Colorado, U.S.A.).

Total ozone (satellite)

21. Observations by a total ozone measuring device carried by a polar-orbiting satellite have the obvious advantages of quasi-global coverage by one and the same sensor (thus being readily comparable). The Backscatter Ultraviolet (BUV) instrument carried by a satellite operated by the U.S.A. gives values of total ozone which are compatible to within 6% of those obtained by Dobson spectrophotometers.

Surface ozone

22. Since this involves a simple in-situ chemical analysis process, relatively inexpensive automatic instruments are available for measuring the amount of ozone at or near the surface.

Vertical distribution of ozone

23. Balloon-borne ozonesondes are probably the most reliable method at present of measuring the vertical distribution of ozone, but the highest altitude reached is usually about 30 km, or somewhat above the level of maximum ozone concentration. Fortunately, remote sensing from satellites is currently capable of providing useful information on the vertical ozone profile down as far as the level of maximum concentration, so that the two techniques are complementary in producing a complete profiles. These sondes and satellite sensors each give a precision of 5 to 10% above 30 km. Rocket-borne ozonesondes are a means of obtaining a homogeneous profile. WMO has organized intercomparisons of ozonesondes and comparisons with satellite-derived data.

24. As a back-up for the ascending/sensing systems mentioned above, it is possible to obtain some indication of the vertical distribution of ozone using an ozone spectrophotometer near sunrise and sunset, the so-called Umkehr technique.

NOTE: In paragraphs 1 - 24 above, the situation as it exists has been stated in a brief, non-technical manner. The next three sections (paragraphs 26 - 89) treat the subject in greater depth, and readers who do not wish to dwell on this are invited to turn to the recommendations on page 33.

II. REVIEW OF CURRENT KNOWLEDGE RELEVANT TO ATMOSPHERIC OZONE

Ozone photochemistry: facts and theories

25. Solar radiation, in particular in the UV region, is the driving force in the ozone chemistry at all heights. The first theory of ozone generation and destruction, which was generally accepted for many years, was that propounded by Chapman in the early nineteen thirties. Only since the mid nineteen sixties was knowledge made more refined, as will be seen from the following paragraphs. Any assessment of the mechanisms leading to the existing ozone distribution, as well as predictions of anthropogenic perturbations in ozone, rest upon adequate knowledge of (a) the solar spectrum, (b) the attenuation of the solar flux caused by absorption and scattering, and (c) the resulting capability to dissociate various gases. These factors are reflected in the recommendations in section VI under the heading "Studies of photochemistry".

26. In order to provide a somewhat more fundamental background in ozone photochemistry for the benefit of those intimately involved in the problem, as well as to inform on the more recent developments, the following represents the very basic photochemistry in symbols and in words.

The Chapman theory

27. Photodissociation of molecular oxygen (O_2) by solar ultra-violet radiation ($h\nu$) at wavelength (λ) less than 242 nm

$$O_2 + h\nu \longrightarrow O + O$$

results in the formation of ozone below 80 km

$$O + O_2 + M \longrightarrow O_3 + M$$

where M is any third body (mainly N_2). The ozone in turn can be dissociated by solar radiation ($\lambda < 320$ nm) and to some extent also by visible radiation

$$O_3 + h\nu \longrightarrow O_2 + O^*$$

where O^* is an oxygen atom in an electronically excited state ($O^* \equiv O(^1D)$), and can enter into a destructive reaction with atomic oxygen

$$O_3 + O^* \longrightarrow 2\,O_2$$

The latter (Chapman) reactions destroy about 20% of the ozone formed.

Hydrogen system

28. The hydrogen system, while of only minor importance in the direct destruction of ozone (it destroys about 10% of the ozone formed, although becomes dominant in this regard above 40 km), is of great indirect importance in ozone photochemistry.

Several reaction schemes have been suggested to account for this influence. One involves the radicals OH and HO_2 that arise mostly from the photochemistry of water

$$H_2O + O^* \longrightarrow 2HO.$$

The following reactions are particularly important above 40 km:

$$HO + O_3 \longrightarrow HO_2 + O_2$$
$$HO_2 + O \longrightarrow OH + O_2$$
$$\text{Net: } O + O_3 \longrightarrow 2\,O_2$$

whereby ozone and one atomic oxygen atom are transformed into two molecular oxygen atoms, and the catalyst (OH) is renewed to repeat the process. In this way one OH radical can be responsible for the destruction of many ozone molecules. OH radicals could be supplied to the stratosphere also when methane (CH_4) (produced principally by bacteria in marsh lands and lakes) diffuses upward and reacts with O^* in the stratosphere to produce the hydroxyl radical (OH)

$$CH_4 + O^* \longrightarrow CH_3 + OH$$

which thereafter follows the above scene. Hydrogen (H), the perhydroxyl radical (HO_2) and OH interconvert very rapidly by reaction with O, so that all three tend to be in a steady state. Depletion of the radicals OH and HO_2 is accomplished principally by

$$OH + HO_2 \longrightarrow H_2O + O_2$$

resulting in the formation of water which can drift down out of the stratosphere. The latter reaction, and its rate, is one of the most important (and sensitive) reactions in the photochemistry of the stratosphere, and hence in the photochemistry of ozone.

Nitrogen system

29. The ozone balance of the stratosphere is maintained principally by the oxidation of nitrous oxide (N_2O) released at the Earth's surface. N_2O is produced by bacterial action of micro-organisms in the ocean and soil (denitrification) and diffuses upward through the troposphere to the stratosphere. It is relatively inert. In the stratosphere

$$N_2O + O^* \longrightarrow 2\,NO$$
$$NO_2 + h\nu \longrightarrow NO + O$$

and the nitric oxide (NO) thus produced catalyzes ozone by

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$
$$\text{Net: } O_3 + O \longrightarrow 2\,O_2$$

where once again ozone and atomic oxygen are transformed to molecular oxygen. The reaction of nitrogen dioxide (NO_2) with the hydroxyl radical OH

$$OH + NO_2 + M \longrightarrow HNO_3 + M$$

forms nitric acid which is eventually washed out of the troposphere and hence represents the major sink of the system. Almost 60% of the ozone formed is believed to be destroyed by this natural system. Other natural, but less important, stratospheric sources of NO include galactic cosmic rays, solar proton events, meteoroides, lightning in the troposphere (with some upward transport of NO through the tropical tropopause), and a downward flux from the winter thermosphere. Furthermore, it should be noted that increased use of fertilizers and increased acidity of rain could enhance the N_2O release from the ground (see Appendix D). Since NO is formed at temperatures exceeding 2000°K by the reactions

$$O_2 + M \longrightarrow O + O + M$$
$$O + N_2 \longrightarrow N + NO.$$

NO is formed in nuclear explosions and also in jet engines, and the latter is thought to be a serious problem in the case of large numbers of high-flying aircraft.

Chlorine

30. Natural chlorine makes only a minor (few percent) contribution to ozone destruction, but the chlorine included in man-made chlorofluoromethanes (CFMs) released into the atmosphere may have a serious effect. In particular, the chlorofluoromethanes $CFCl_3$ and CF_2Cl_2 (also known as Freon 11 and 12 respectively) which are used in refrigeration and as a propellant in various aerosol sprays, are inert in the troposphere but are dissociated at a height of about 30 km (near the height of maximum ozone formation) by ultra-violet radiation in the 180-225 nm "window" between the Schumann-Runge and Hartley absorption bands. The chlorine released by the photolysis destroys ozone by the catalytic chain

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$
$$\text{Net: } O + O_3 \longrightarrow 2\,O_2$$

with the same consequences as previously. The ClO_x catalytic efficiency is reduced by the reaction

$$ClO + NO \longrightarrow NO_2 + Cl$$

followed by

$$NO_2 + h\nu \longrightarrow NO + O.$$

The chlorine sink is HCl (hydrogen chloride, also known as hydrochloric acid) which

is formed primarily through the reaction of chlorine with methane and the perhydroxyl radical

$$CH_4 + Cl \longrightarrow HCl + CH_3$$
$$HO_2 + Cl \longrightarrow HCl + O_2.$$

The balance between the chlorine radicals (Cl and ClO) and HCl is determined by the above two reactions in competition with the recycling step

$$HCl + OH \longrightarrow H_2O + Cl.$$

The latter reaction, and its rate, is another very important (and sensitive) reaction in ozone photochemistry. It might be noted that whereas the chlorine catalysis of ozone is about six times as efficient as the nitric oxide catalysis of ozone, the conversion to "intert" hydrogen chloride is also more efficient than the conversion to "inert" nitric acid, so that the two processes are in fact comparable in overall efficiency. Interaction of the nitrogen and chlorine systems comes about through

$$ClO + NO \longrightarrow ClNO_2$$

forming nitryl chloride and

$$ClO + NO_2 \longrightarrow ClNO_3$$

forming chlorine nitrate. The latter process is particularly important because it removes radicals from both the chlorine and nitrogen cycles, and it is not yet certain how much this reaction reduces the ozone depletion deduced from the other reactions (see next paragraph).

Chlorine nitrate effect

31. The U.S.A. National Academy of Sciences (NAS) report of 1976, based on recent studies of the chlorine nitrate reactions, estimated that this effect reduces the degree of ozone depletion due to other reaction from a projected 14% to 7.5%, i.e. by a factor of 1.85. Model calculations and a few measurements, however, suggested that the chlorine nitrate concentration is less than previously thought, apparently because the reaction

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M$$

is much slower than the reaction

$$OH + NO_2 + M \longrightarrow HNO_3 + M.$$

Recent measurements and calculations suggest that in fact the chlorine nitrate chemistry reduces the degree of ozone depletion from 14% to 10-11 percent (rather than 7.5%). It must be stressed that there is still great uncertainty concerning the magnitude of the chlorine nitrate effect, and more measurements and investigations are needed.

Bromine

32. Other halogens, bromine in particular, react in a manner similar to chlorine and thus have the same ozone-destroying possibilities, although being perhaps even

more efficient than chlorine in this regard. Bromine could be delivered through the decomposition of methyl bromide (CH_3Br), most of which is believed to be produced by marine algae. However, a small but growing man-made source of CH_3Br exists as a result of fumigation processes in agriculture, although the latter is believed to be small compared with the chlorofluoromethane release.

Relevant processes in the troposphere

33. The amount of ozone in the troposphere is small by comparison with the stratosphere, but nevertheless constitutes a not insignificant part of the total ozone. Consequently changes in tropospheric ozone will result in changes in total ozone to an extent which cannot be ignored.

34. Sources of tropospheric ozone are twofold; firstly the downward transport from the stratosphere, in particular in middle and high latitudes (this is a natural source which is not likely to undergo systematic changes in the future). Secondly, there is the photochemical production of ozone in the troposphere, in "clean" air as well as heavily polluted air. Whereas some information on these two sources is available, our knowledge about tropospheric ozone is incomplete, particularly as regards the photochemical production.

35. Photochemical production of ozone in the troposphere is caused partly naturally and partly as a result of human activities. As in the stratosphere, OH and HO_2 play important roles in the ozone chemistry. In clean air hydroxyl originates from the decomposition of water vapour by excited atomic oxygen

$$H_2O + O^* \longrightarrow OH + OH.$$

In turn, HO_2 is formed when naturally occurring methane is decomposed through reaction with OH. HO_2 is of particular importance since it converts NO to NO_2

$$NO + HO_2 \longrightarrow NO_2 + OH$$

whereby the production of odd oxygen through photodissociation of NO_2 is increased.

36. Under certain conditions, the production of ozone in the lowest layers may be drastically increased in heavily polluted urban and industrial areas, where a new source of odd hydrogen, the hydrocarbons, is emitted as a result of consumption of fossil fuels. The HO_2 content (mainly responsible for the conversion of NO to NO_2 in the "clean" atmosphere) is increased by orders of magnitude as a result of oxidation of hydrocarbons. In addition, other radicals, of the type $R\dot{O}_2$, which also promote the $NO \longrightarrow NO_2$ conversion, are produced. Ozone produced locally in this way may be transported over long distances and mixed with the surrounding air.

Some recent assessments

37. The calculated ozone reduction is extremely sensitive to any tropospheric sink for the chlorofluoromethanes. For example, only about 1% of the CFMs in the atmosphere is dissociated each year, so that if there were an inactive sink that removes 2% of the CFMs each year without destroying ozone, then the ozone reduction

would be only one-third of the estimate without such a sink. On this basis, the NAS report reduced the eventual ozone depletion from 7.5% to 6.0% largely on the assumption of some CFM absorption by sea water, followed by an unknown degradation process. The presence of such an inactive sink could be verified if accurate estimates of CFM release and the amount of CFM in the atmosphere could be obtained. The latter parameters are particularly uncertain, with considerable controversy regarding the existing gradient of CFM between the northern and southern hemispheres. More work needs to be done on this topic too.

38. The importance of carbon tetrachloride (CCl_4) in the ozone depletion problem also remains controversial because of the uncertainty as to how much is natural and how much is man-made. Even though the anthropogenic release of CCl_4 should be decreasing, the Adrigole (Ireland) surface measurements continue to show that it is increasing in the atmosphere at the same rate as $CFCl_3$. Until the CCl_4 problem is resolved, uncertainty is bound to surround the ozone depletion problem.

39. A speculative positive feedback process involves an increase in the upwelling of water vapour through the tropical tropopause due to warming of the tropopause because of redistribution of the ozone to lower levels owing to destruction of ozone at around 30 km by dissociation of CFMs. This would lead to more OH radicals

$$H_2O + O^* \longrightarrow 2\,OH$$

and hence to catalytically active chlorine through

$$HCl + OH \longrightarrow H_2O + Cl.$$

The only long-term stratospheric water vapour measurements available at Washington, D.C., indicate a 30% increase in stratospheric (14-26 km) water vapour between 1964 and 1969, little change between 1970 and 1974, and a sharp drop since 1974 back to almost the 1964 level.

40. A few additional facts which became available at the Logan (Utah, U.S.A.) conference just at the time of release of the NAS report in September 1976 put in question several of the assumptions made in the NAS report and as already noted (see paragraph 31) have tended to support an even greater reduction in ozone than the projected figure of 7.5% given in the NAS report.

41. For instance, measurements by Dr. Rasmussen of Washington State University of chlorine compounds in the atmosphere showed a greater level of CFMs, carbon tetrachloride, and other potential ozone-reducing compounds. These findings were consistent with the major release of these substances by the industrialized nations. The findings also strongly suggested that much of the atmospheric load of carbon-tetrachloride is due to human activity. This represents an additional source of ozone depletion by the human race.

42. Of similar import were the findings of Dr. Anderson of the University of Michigun, who presented the first simultaneous measurements of chlorine atoms and chlorine oxides at different altitudes in the stratosphere. The findings of these chemical fragments in amounts close to those predicted by theory provides important confirmation of the general theory of ozone depletion by chlorine-containing molecules, including man-made CFMs.

43. Laboratory measurements of the absorption of ultraviolet light by CFMs at stratospheric temperatures were also reported. If these values are used instead of those assumed previously, the depletion of ozone would be greater by one-half to 1% than the NAS estimate. Previously it had been argued that this correction would reduce the degree of ozone depletion.

Distribution of ozone in the atmosphere, with particular reference to certain recorded man-made and natural events

44. Since the main topic underlying the discussion is the possible effect of chlorofluoromethanes and other man-made species on atmospheric ozone, it is necessary to have a clear picture of the global ozone distribution and its natural variability.

45. Although some early observations of total ozone were made as far back as 1908, and routine Dobson spectrophotometer measurements began at Arosa and Tromso in the 1930s, it was not until the International Geophysical Year (1957) that sufficient observations became available to make possible an approximative global analysis of the total ozone distribution. Figure 1 shows the average annual total ozone distribution over the 10-year period 1957-1967, while Figure 2 depicts the variation in

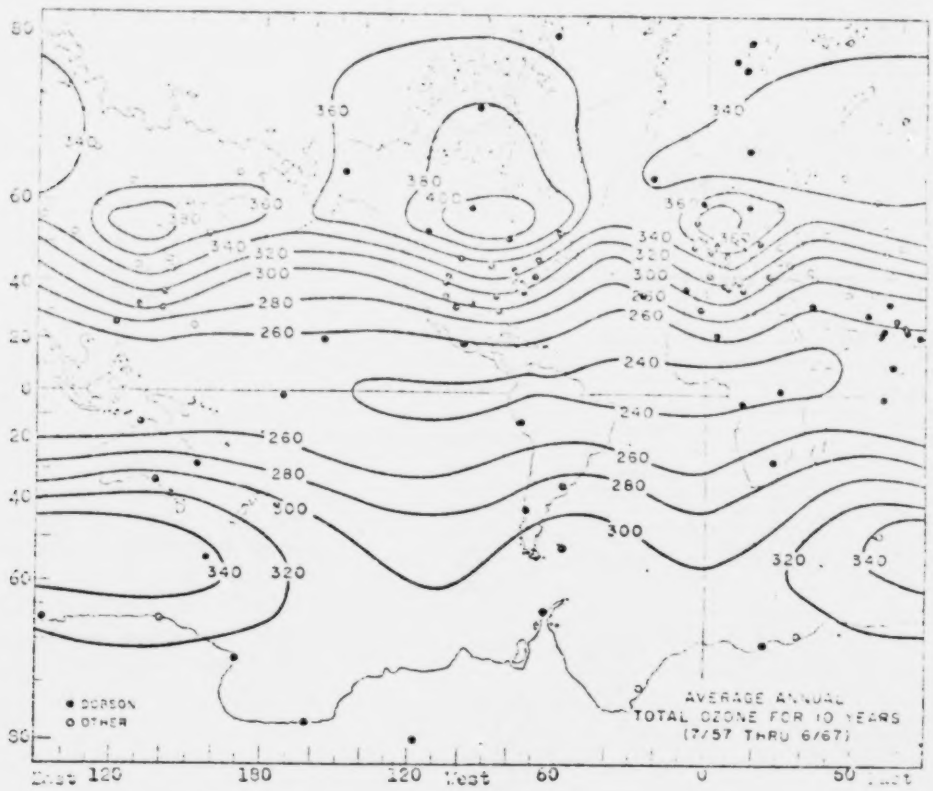

FIGURE 1

Global average total ozone distribution for the years 1957-1967, expressed in m-atm-cm (Dobson units). The dots and small circles indicate station locations. (London & Bojkov)

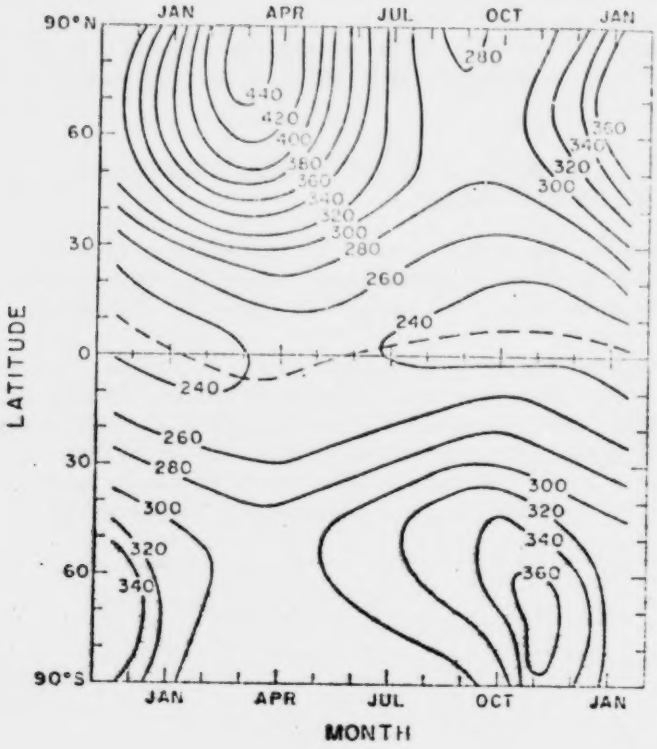

FIGURE 2

Average variation in total ozone (m-atm-cm) by latitude and month, based on observations during 1957-1967. (London & Bojkov)

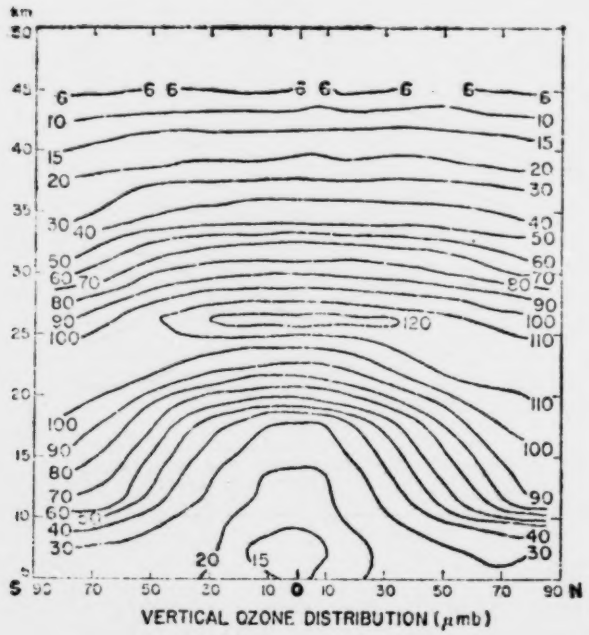

FIGURE 3

Mean variation of vertical ozone distribution (partial pressure in μmb) as a function of latitude based on 8,500 Umkehr profiles and ozone soundings taken between 1956 and 1966. (Bojkov)

total ozone as a function of latitude and month during the same period.

46. Figure 3 and Table 2 indicate the mean meridional distribution of ozone. It can be seen that in the lower and middle stratosphere the fractional ozone content increases from the Equator toward the poles, whereas in the upper stratosphere it diminishes slightly toward the poles, so that in equatorial regions 38% of the total ozone is found above 28 km (where the greatest photochemical activity takes place) whereas in polar regions only 18% (less than half) is found above this level.

TABLE 2

Ozone in various layers as a percent of total ozone at given latitudes (Bojkov)

Layer (km approx.)	0-10	10-15	15-19	19-24	24-28	28-33	33-38	above 38 km.
Latitude: polar	10	17	18	19	17	10	5	3.5
middle	9	11	14	20	20	14	7	4.5
subtropical	8	6	9	20	25	17	9	5.4
equatorial	4	3	5	19	30	21	10	7.3

47. Figure 4 shows the variability of the ozone partial pressure in terms of its standard deviation. The variability is largest in the low stratosphere in middle and high latitudes, and decreases to a relatively small value at all levels in the tropics. In other studies it is indicated that the ozone partial pressure turns out to be most highly correlated with the total ozone in the column at heights between 10 and 20 km in middle and high latitudes, i.e., changes in total ozone mainly

(continued on p.18)

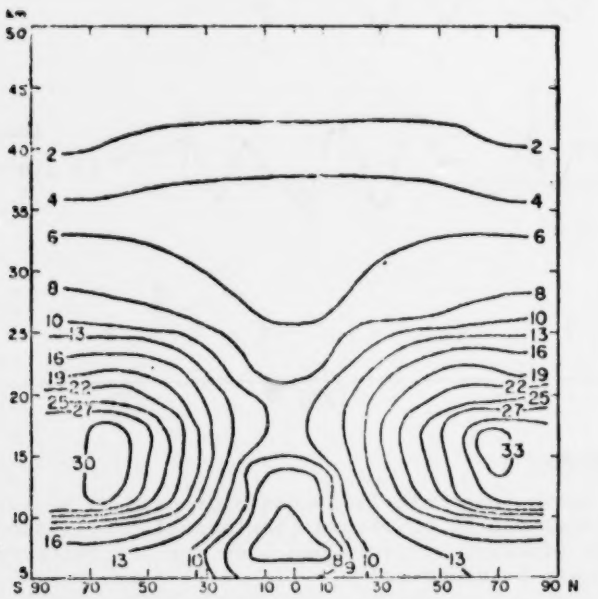

FIGURE 4

Standard deviation of ozone partial pressure (μmb) as a function of latitude and height. Large values indicate high variability. (Bojkov)

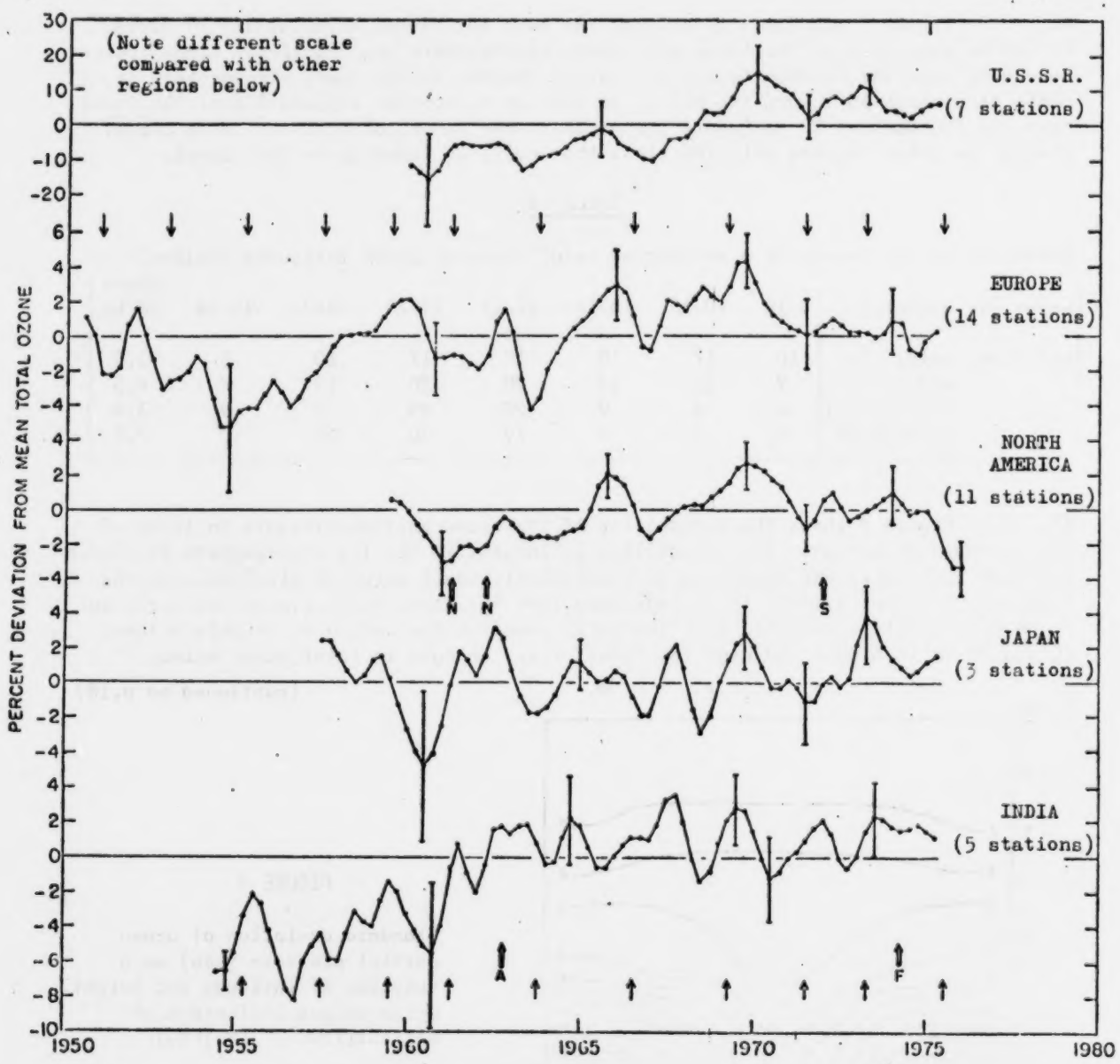

FIGURE 5

Time variation in total ozone in north temperate latitudes expressed as a percentage deviation from the mean for the total length of record (the annual oscillation has been removed). A 1-2-1 smoothing (divided by four) has been applied twice to the successive seasonal values. (Angell & Korshover)

Vertical bars represent two standard errors of estimate based on individual station values within the regions. Single-shafted arrows indicate occurrence of quasi-biennial west wind maximum at 50 mb in the tropics;

A = Eruption of Mt. Agung (Indonesia) F = Eruption of Mt. Fuego (Guatamala)
N = Large nuclear explosions S = Large solar proton event.

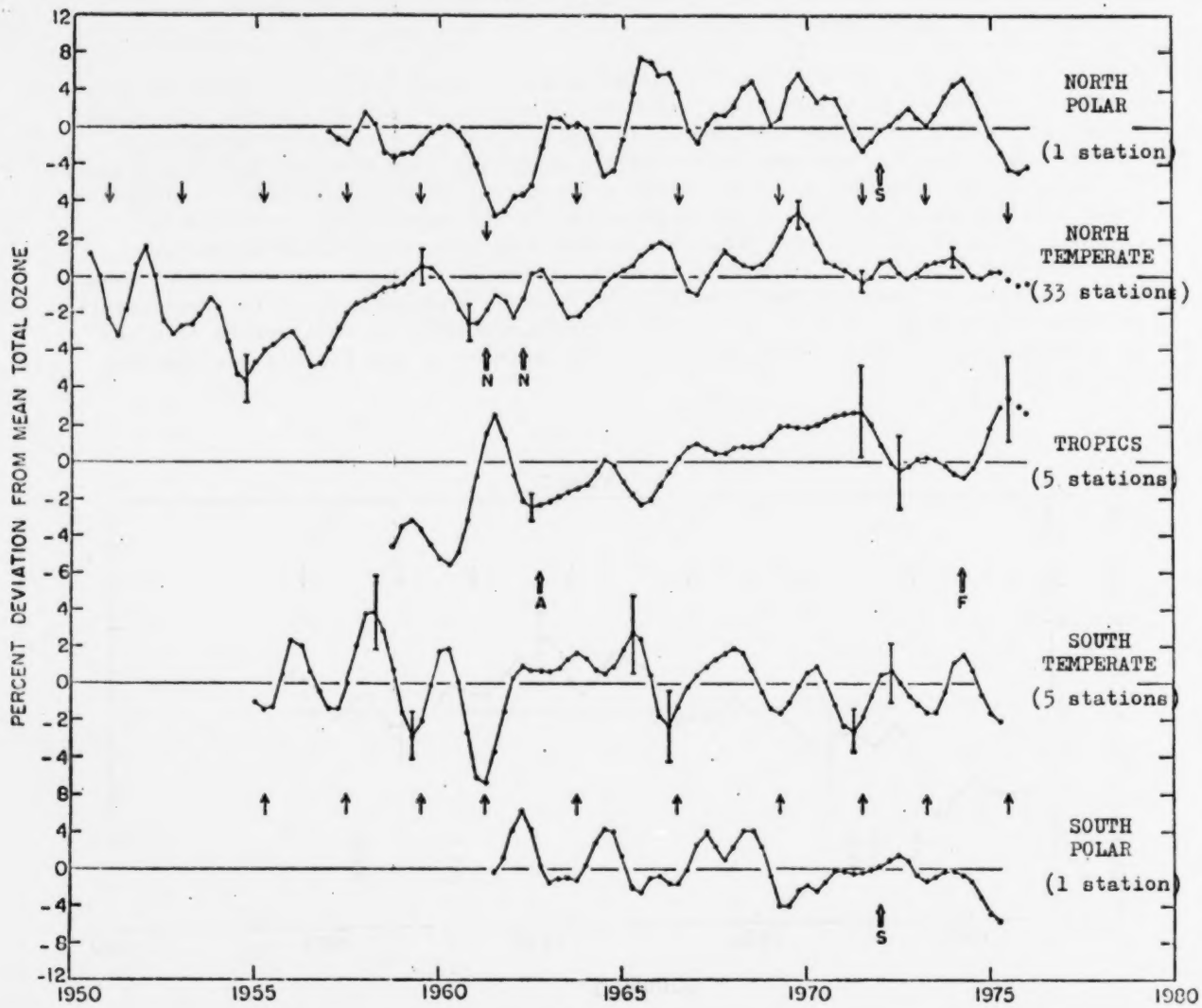

FIGURE 6

Time variation in total ozone in global climatic zones expressed as a percentage deviation from the mean for the total length of record (the annual oscillation has been removed). A 1-2-1 smoothing (divided by four) has been applied twice to the successive seasonal values. (Angell & Korshover)

Vertical bars represent two standard errors of estimate based on individual station values within the regions. Single-shafted arrows indicate occurrence of quasi-biennial west wind maximum at 50 mb in the tropics;

A = Eruption of Mt. Agung (Indonesia) F = Eruption of Mt. Fuego (Guatamala)
N = Large nuclear explosions S = Large solar proton event.

reflect changes in ozone amount in this layer. In the upper stratosphere these correlations are very weak, and in middle latitudes there is even a region where the correlation is negative, that is, if the total ozone increases, the ozone amount in the region near 50 km tends to decrease.

48. Figure 5 shows the time variation in total ozone for those regions in north temperate latitudes possessing adequate data. The annual oscillation has been eliminated and a 1-2-1 smoothing (divided by 4) applied twice to successive seasonal values. Note that the ordinate is percentage deviation from the mean with the scale for the U.S.S.R. stations quite different. The number of stations with the given regions is indicated at the right. Figure 6 shows the total ozone variation for climatic zones where, in north temperature latitudes, the regional averages have been weighted subjectively according to area, number of stations and quality of data (the weighting is Europe 3, North America 3, Japan 1, and India 1, filter ozonometers are excluded). Figure 7 shows the derived world-wide trend in total ozone obtained by weighting the climatic zones of Figure 6 by the area of the Earth's surface they represent.

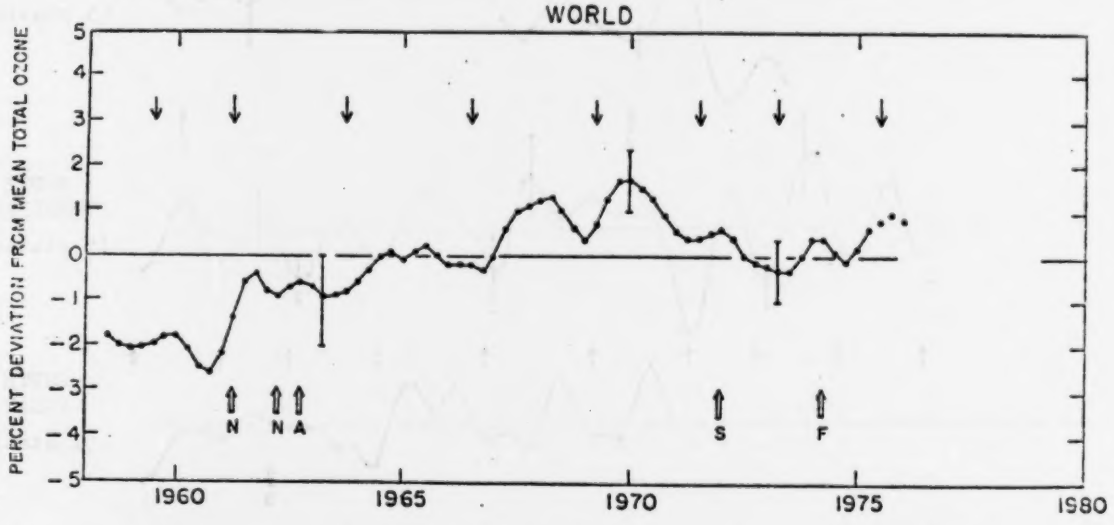

FIGURE 7

Estimated time variation in global total ozone expressed as a percentage deviation from the mean for the total length of record (the annual oscillation has been removed). A 1-2-1 smoothing (divided by four) has been applied twice to the successive seasonal values. (Angell & Korshover)

Vertical bars represent two standard errors of estimate based on individual station values. Single-shafted arrows indicate occurrence of quasi-biennial west wind maximum at 50 mb in the tropics;

A = Eruption of Mt. Agung (Indonesia) F = Eruption of Mt. Fuego (Guatamala)
N = Large nuclear explosions S = Large solar proton event.

49. In general, based on the period of available observation (which is really much too short for the accurate delineation of trends), the total ozone increased during the 1960s, peaked about 1970, then declined about half as much between 1970 and 1973 as it had risen during the 1960s, and since 1973 has remained essentially unchanged. Note, however, that Japan and India do not exhibit this variation, and in the Southern Hemisphere there is evidence of a slight decrease in total ozone over most of the period of record. The single-shafted arrows in Figures 5-9 indicate the time of quasi-biennial west wind maximum at 50 mb (20 km) in the tropics, and it can be seen that whereas this oscillation is most obvious in total ozone in south temperate latitudes, it also permeates most other climatic zones. It is emphasized, however, that these variations and trends must be accepted with great caution since the total ozone stations are mostly confined to the continents so that changes in circulation patterns could affect the results.

50. There is evidence, particularly in Europe, that the amount of ozone peaked about 1960 as well as in 1970, and both times are near the time of sunspot maximum. It is not at all certain that there is a real relation here, but if there is, this would explain the levelling-off of the ozone in recent years (the present sunspot minimum is unusually prolonged) and we should expect the ozone to increase slightly in the near future.

51. The double-shafted arrows labeled N in Figures 5-9 indicate the time of large nuclear explosions at Novaya Zemlya (75°N) in the autumn of 1961 and 1962. It is known that nitric oxide (NO) is produced by the high temperatures in a nuclear explosion, but on the other hand as the fireball cools by radiation emission, that radiation between 185 and 242 nm would dissociate oxygen and create ozone in a region surrounding the explosion. Hence, for a few days following the explosion one might even find an enhancement rather than reduction in total ozone downwind of the detonation site. After a week or two, though, the nitric oxide effect should dominate. Whilst the magnitude of the above explosions suggests a large production of nitric oxide in the low and middle stratosphere, the nitric oxide would not (basically) have been able to react with, and decrease, ozone for a few months due probably to circulation specifics. The model calculation of Chang indicated a 3-4% decrease in hemispheric total ozone due to these explosions, but such an effect is not obvious from Figures 5-7. Even though the picture is clouded by quasi-biennial oscillation, it is difficult to see how the nuclear-induced reduction in total ozone in northern latitudes could have exceeded 1%. The discrepancy between observation and theoretical model has not yet been explained.

52. The double-shafted arrow labeled A in Figures 5-9 indicates the time of the eruption of Mt. Agung in Bali, Indonesia (8°S) in the spring of 1963. At the time of the eruption the strong quasi-biennial oscillation in total ozone in south temperate latitudes ceased, and the ozone amount remained at a relatively high level until 1965, when the oscillation resumed, though not with its original vigour. It is tempting to relate the breakdown of the quasi-biennial oscillation in total ozone to the eruption, but the quasi-biennial oscillation in zonal wind in the tropical stratosphere increased from 2 to nearly 3 years at this same time, which seems a more likely cause for the breakdown in the total ozone oscillation. In any case, there is no evidence that the hydrogen chloride and water vapour emitted by Mt. Agung reduced the ozone column, indeed no hydrogen chloride was observed in the stratosphere from the eruption of Mt. Fuego in Guatemala in 1974, which may also have been the case with the Mt. Agung eruption. (continued on p.23)

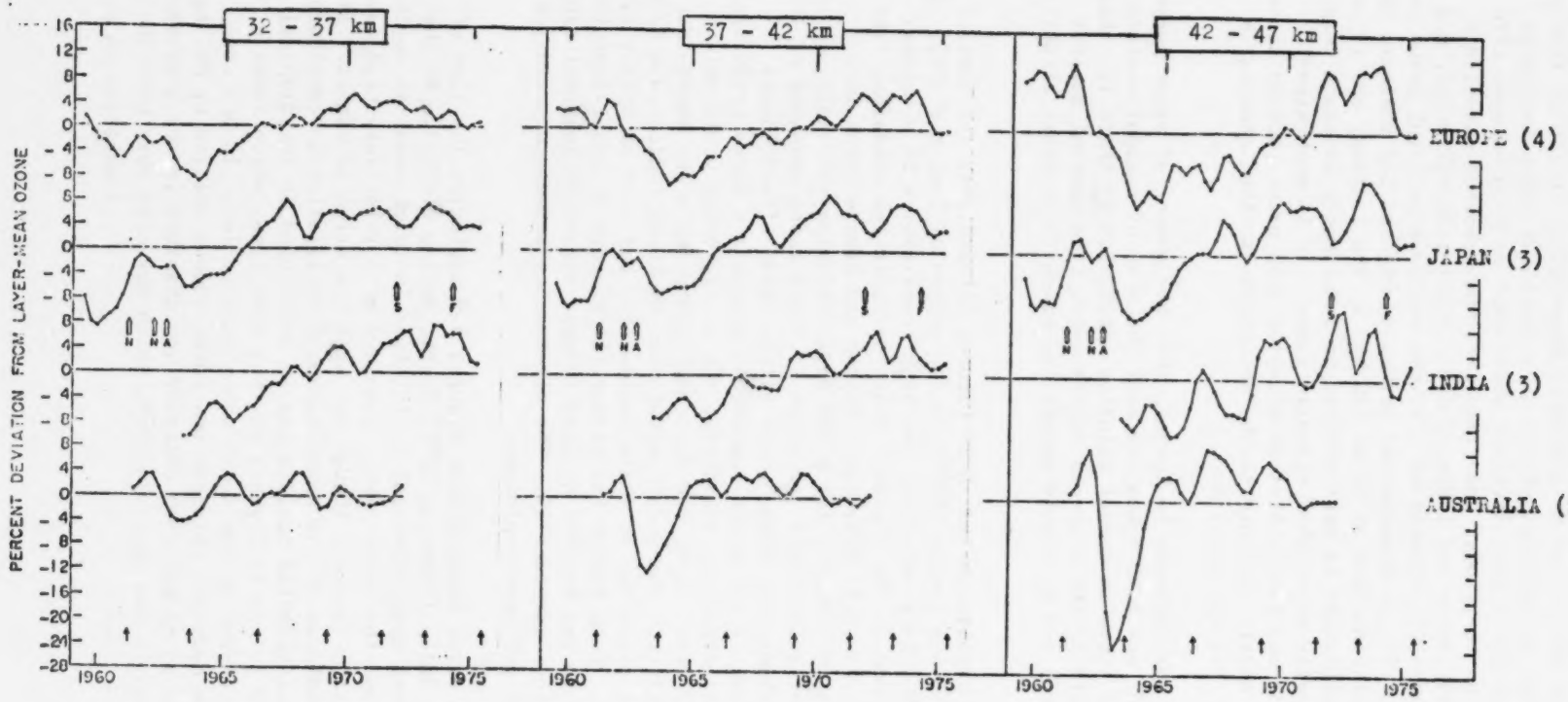

FIGURE 8

Time variation of ozone (percentage deviation from the mean) in different layers as determined from Dobson spectrophotometer Umkehr measurements at stations in Europe, Japan, India and Australia. (Angell & Korshover)

The number of stations is indicated in brackets. Single-shafted arrows indicate occurrence of quasi-biennial west wind maximum at 50 mb in the tropics;

A = Eruption of Mt. Agung (Indonesia)
F = Eruption of Mt. Fuego (Guatamala)
N = Large nuclear explosions
S = Large solar proton event.

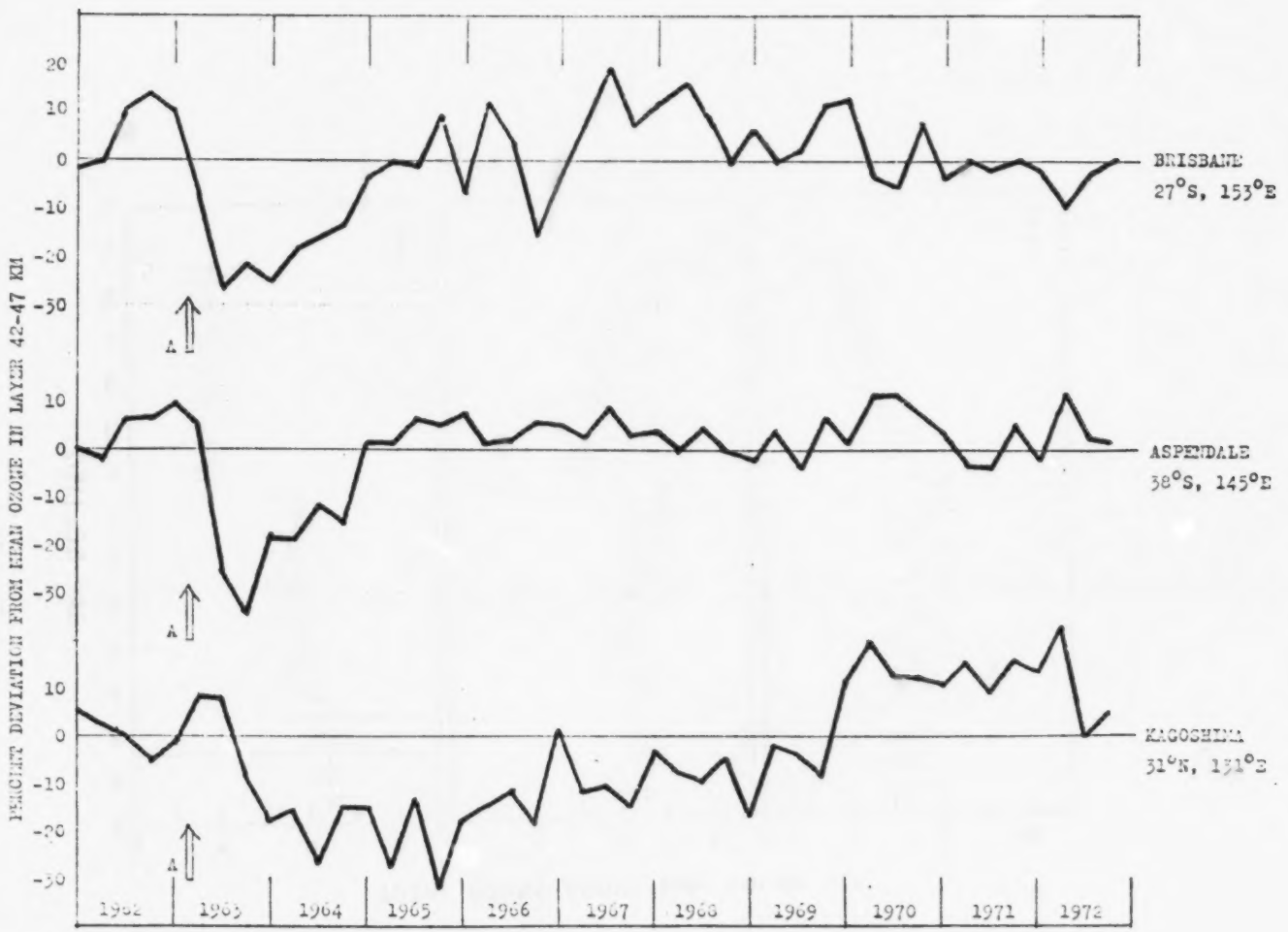

FIGURE 9

Indicated variation (percentage deviation from the mean) of ozone in the 42-47 km layer at Brisbane, Aspendale and Kagoshima. The annual oscillation has been eliminated, but the seasonal data are unsmoothed. Double-shafted arrow "A" marks the time of eruption of Mt. Agung (8°S, 115°E). (Angell & Korshover)

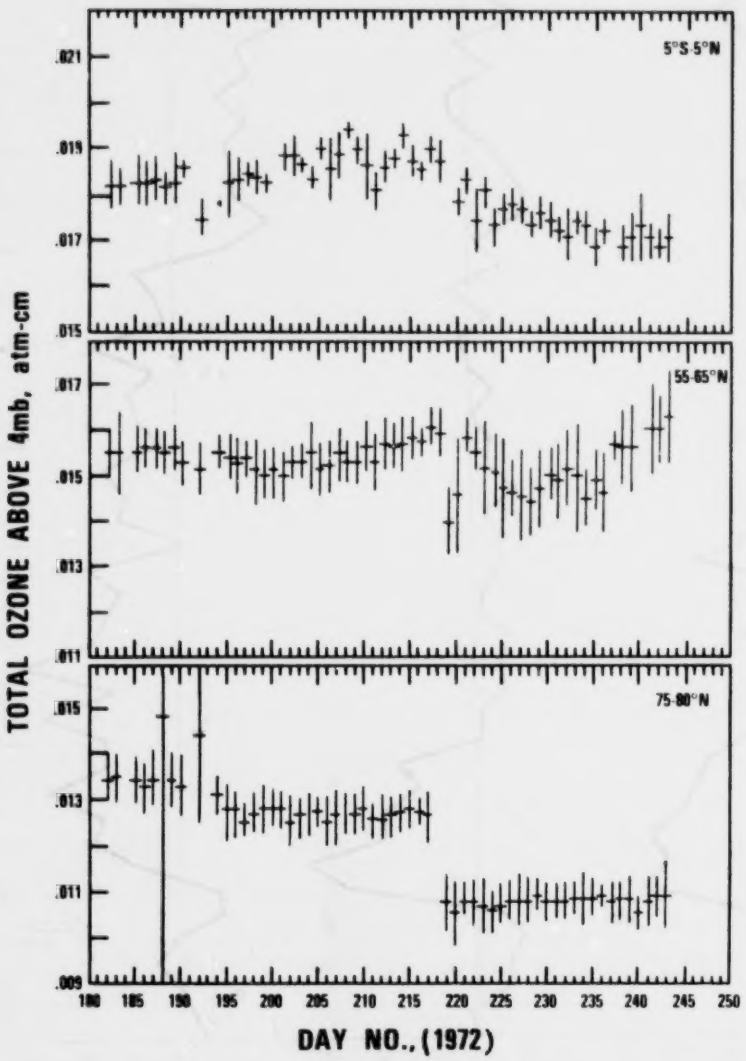

FIGURE 10

Time variation of total ozone above 4 mb (about 40 km) as a function of latitude, as measured by the BUV instrument on Nimbus 4. A large solar proton event occurred on day 218. (Angell)

53. High energy solar proton events have the capability of producing nitric oxide (NO) through ionization of nitrogen by means of secondary electrons formed by energetic protons. The largest such event in the last 15 years (there apparently was an even larger event in 1959) occurred on 4 August 1972 (double-shafted arrow labeled S in Figures 5-8). The top diagram of Figure 6 indicates no obvious effect of the solar proton event on total ozone at the north polar region (Resolute), very close to the magnetic pole where any effect on the ozone amount should be maximal (Resolute is the only high latitude Arctic station). (However see also paragraph 55).

54. Figure 8 shows the time trend in ozone for the height intervals 32-37, 37-42, and 42-47 km as derived from Umkehr measurements in the 4 regions (Europe, Japan, India, Australia) presently reporting such measurements. The ozone trend at these elevations is generally similar to the trend in total ozone, although the reduction in ozone after 1970 is not so obvious at the high levels. It is not certain whether the tendency for the percentage variation to increase with height is real, or inherent in the analysis technique. A striking feature is the indicated decrease in ozone above 35 km at Australian stations following the eruption of Mt. Agung in 1963. Figure 9 shows that the decrease occurred slightly later at sites further removed (latitudinally) from the eruption site, as though a dust cloud were spreading meridionally. Since the height of the volcanic dust cloud could hardly have exceeded 25-30 km, and yet the magnitude of the ozone reduction is indicated to increase with height up to 50 km, it is probable that the indicated ozone reduction is fictitious rather than real, demonstrating that Umkehr observations in a turbid atmosphere should be scrutinized carefully.

55. The Nimbus 4 ozone data are in the process of being re-reduced (see paragraph 101) and until this is accomplished, and new analyses made, it is inappropriate to review these data. Nevertheless, it must be noted that the BUV instrument on Nimbus 4 (Figure 10) has suggested a dramatic consequence of the solar proton event of 1972 on total ozone amounts above the level of 4 mb (40 km) at high geomagnetic latitudes. The percentage decrease in ozone is indicated to be at least 15% at these high levels (4 August is day 218), but only slightly more than 1% for the total ozone column, a value which would be lost in the noise level of the Dobson data at Resolute. Thus, we appear to have here the first "hard" evidence for ozone reduction by nitric oxide.

III. SOME CONSEQUENCES OF INCREASING AMOUNTS OF MAN-MADE TRACE GASES IN THE ATMOSPHERE

Consequences on the ozone layer

56. There has already been considerable research conducted into the direct injection of NO_x into the stratosphere by fleets of supersonic aircraft and the consequent effect on the ozone layer. Although there are considerable uncertainties in both measurements and theory (in the latter case being of about a factor of two), the role of NO_x is sufficiently well established to be able to state with reasonable confidence that:

- currently planned SSTs, due to their lower flight altitudes of 17 km and their limited numbers (fewer than 50 projected) are not predicted to have an effect that would be significant or that could be distinguished from natural variations;

- a large fleet of supersonic aircraft flying at greater altitudes is predicted to have a noticeable effect on the ozone layer, and permissible total emission levels may have to be defined by international agreement.

57. A theory has recently been propounded that increased use of agricultural fertilizers and/or of nitrogen-fixing vegetation might affect the nitrogen cycle and result in an increase in the amounts of nitrous oxide (N_2O) released from the surface into the atmosphere. This would then lead to an increase of NO_x in the stratosphere and hence to a decrease in the ozone amount. This source of N_2O might also be stimulated by increases in the acidity of rain.

58. Because of the extreme complexity of this problem, involving as it does the whole global nitrogen cycle, uncertainties regarding the consequences on the ozone layer are still very great. Although there is no likelihood of a significant change in the ozone layer in the near future as a result of changing agricultural practices, the matter deserves thorough study because of the importance of fertilizers in food production and the substantial long-term effects which some scientists consider to be possible (see also Appendix B).

59. Prediction of the degree of ozone depletion resulting from a given rate of release of chlorofluoromethanes (CFMs) into the atmosphere must be made using atmospheric models, and so far the model generally employed has been a 1-D model which, although permitting rather complex photochemical reactions to be incorporated, simplifies atmospheric transport and diffusion (see also Appendix C).

60. The predicted effect on the ozone layer of release of CFMs will of course depend upon the scenario of CFM release, and for illustrative purposes the one chosen here is that used in the NAS report, namely continued production and release of CFMs at the 1973 rate.

61. On this basis, the ultimate "peak" depletion of ozone is predicted in the NAS report to amount to between 6 and 7.5 percent (the lower figure assuming that a small percentage of the CFMs is absorbed by the surface layer of the oceans); 95% confidence limits lie between 2 and 20 percent. The predicted time taken to reach half the peak (i.e. 3 to 3.75 percent reduction of ozone) is 40 to 50 years, so that by the year 2000 the reduction would be at most 2% and therefore possibly difficult to detect from the total-ozone observation network.

62. If the CFM release were terminated at a given moment, the maximum reduction in ozone would not be attained until about 10 years thereafter, and an additional 60-70 years would be required to recover one-half of the maximum loss. Each year of CFM release at the 1973 rate would increase the peak reduction in ozone by about 0.07%.

63. The above scenario is not the only one. Most predictions suggest a somewhat larger ozone reduction. At present one of the most critical factors is the effect of chlorine nitrate ($ClONO_2$) on ozone reduction. As has already been stated (see paragraph 31), the NAS report reduced the maximum ozone reduction from 14% to 7.5% (a factor of 1.85) on the assumption that chlorine nitrate is relatively stable and hence ties up an appreciable fraction of the chlorine radicals which catalytically destroy ozone. Recently there have been both measurements and calculations that suggest that chlorine nitrate is not quite so important in this regard, and that chlorine nitrate chemistry should reduce the peak ozone depletion from 14% to only 10 or 11%.

64. The stability of chlorine nitrate was somewhat of a surprise. The possibility must be considered that other photochemical surprises are in store. Probably the one other most critical factor is the possibility of a tropospheric sink for the CFMs. Since only about 1% of the CFMs are dissociated each year, a small tropospheric sink would have tremendous impact. For example, if a tropospheric sink accounted for only 2% of the CFMs released, the peak ozone reduction would be reduced by two thirds. Direct measurement of a tropospheric sink is not possible because both the CFM release to the atmosphere and the atmospheric burden of CFMs is imprecisely known.

65. An important aspect of the hypothesized reduction in ozone due to CFM release is shown in Figure 11. This diagram presents the expected percentage reduction in ozone, as a function of height, for the years 1972, 2000 and 2025. The reduction is strongly peaked near a height of 40 km, i.e. near the region where the CFMs dissociate most rapidly and where ozone is preferentially formed. According to this diagram, the direct measurement of a reduction in ozone due to CFMs could best be carried out near a height of 40 km. This is too high for most ozonesondes, but BUV satellite data are good and Umkehr measurements are relatively precise if correctly taken. Some of the available Umkehr measurements (Fig. 8) show only slight evidence of a recent ozone decrease at these heights, but considerable evidence of an ozone <u>increase</u> at these heights between about 1963 and 1973.

Consequences on climate

66. Any consideration of the possible influence on the climate of an eventual ozone depletion or of CFMs released in the atmosphere must take account of the fact that there have obviously been naturally-caused climate changes in the past, and it seems likely that there will be similar patterns of change in the future. The long-term record of the Earth's climate has been reconstructed from studies of ocean and lake sediments, the location of ancient glacial moraines, the chemistry of ice cores taken from Greenland and the Antarctic, and so forth, and it now appears that the most pronounced changes in the past million years or more might have been associated with changes in the Earth's axis of rotation and its orbit around the sun. These quasi-periodic alternations between major glaciations and interglacials (such as the present) occur with periods ranging from 25,000 to 100,000 years. While there are apparently periodicities with shorter time scales, their amplitudes are small relative to the larger and more or less random fluctuations of the weather and climate, and it is not possible at this time to predict naturally-induced climate changes for the next year, decade, or century with any useful degree of confidence.

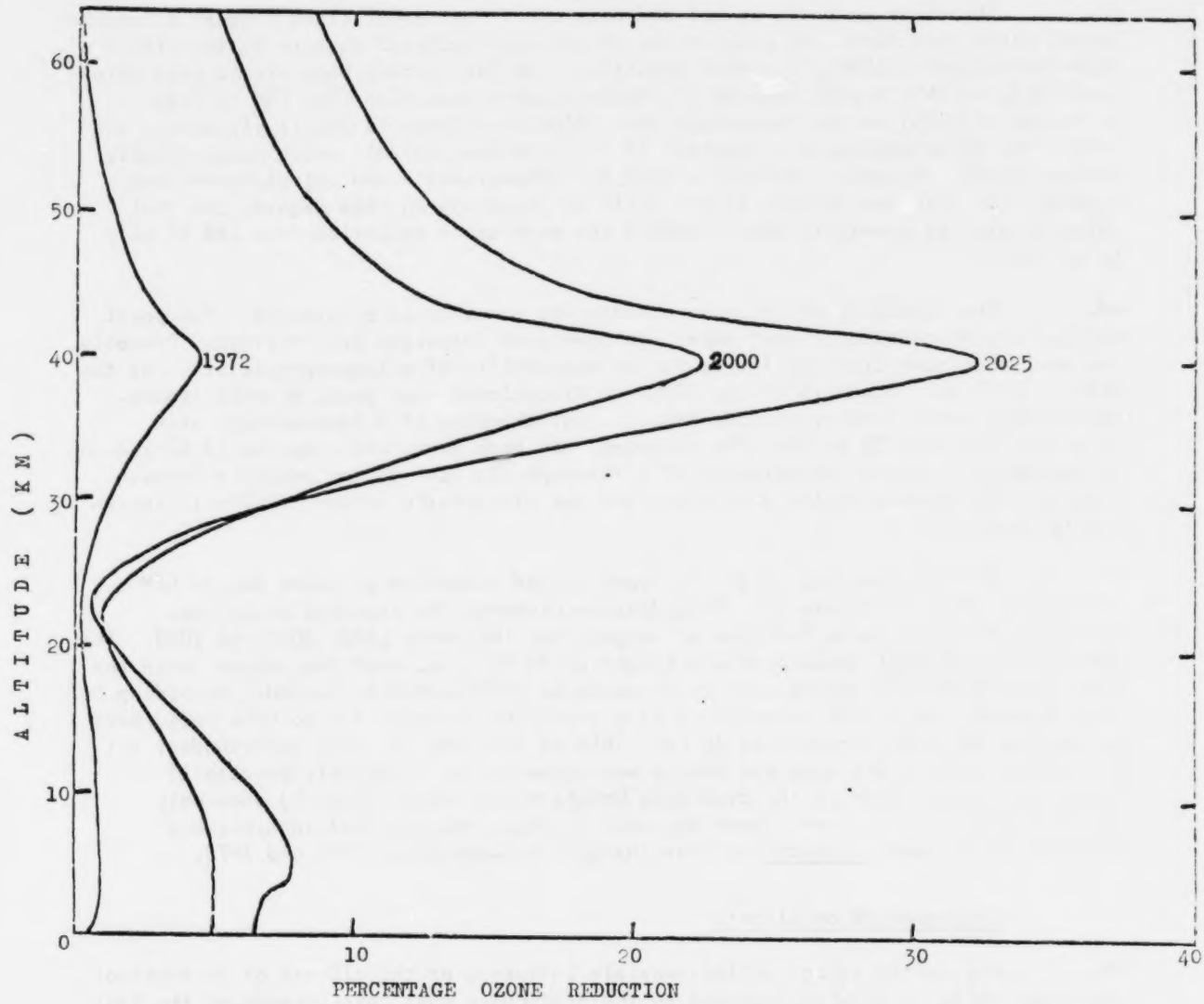

FIGURE 11

Percentage ozone reduction resulting from the release of chlorofluoromethanes at the 1975 rate, as a function of height. Indicated are the model results for the years 1972, 2000 and 2025.
(After Crutzen)

Climatological consequences of possible ozone depletion

67. Because solar ultraviolet radiation is very strongly absorbed by ozone, the temperature of the stratosphere is largely maintained by a balance between absorption of solar radiation by ozone and emission of atmospheric infra-red radiation by ozone, carbon dioxide and water vapour. Any change in the stratospheric heating rates will have a direct influence on the temperature distribution in the stratosphere and possibly in the troposphere, and these temperature changes will have an effect on the patterns of atmospheric circulation and hence on weather and climate. Such thermodynamic and dynamic changes will themselves have significant interactions or feedback on the stratospheric composition.

68. A depletion of ozone due to its reaction with the dissociation products of CFMs or with NO_x will result in a decrease in the temperature of the stratosphere, since ozone absorbs strongly the solar ultraviolet radiation in the 200 to 300 nm part of the spectrum, as well as some visible radiation, thus causing the relatively high temperature of the stratosphere between about 30 and 60 km. Theoretical calculations using a radiative-convective model of the atmosphere, based on a decrease of total ozone of 7% due to CFMs (corresponding roughly to one prediction of a steady-state situation with CFM production at the 1972 level), indicate that the cooling at 40 km would be between about 4 and 8°C, but that lower in the stratosphere at 20 km the change would be only about 1°C and of indeterminate sign.

69. Because of the complexity of stratosphere-troposphere interactions it is not possible to infer with any reliability what the full consequences of these changes would be on the Earth's climate. Nevertheless it may be of interest to note in passing that the same radiative-convective model calculations were extended to the surface to determine what change in surface temperature would result from the same 7% decrease in total ozone. The change was negligible, being a few hundredths of a degree and of indeterminate sign. The reason for this is that there are two opposing and roughly equivalent processes at work; the ozone decrease lets some more solar radiation reach the surface, causing a small warming, and at the same time cools the middle and upper stratosphere as has been seen and lowers the emissivity there, thus decreasing the downward flux of the infra-red radiation from the stratosphere and causing a small cooling. It thus seems that a small percentage of ozone decrease by itself has only a small influence on the globally averaged surface temperature, although it has recently been postulated that enhanced heating of the stratospheric sulphate layer (due to reduction of the ozone above) might lead on balance to a slight surface warming because of the increased downward flux of infra-red radiation from this layer.

Climatological consequences of increased chlorofluoromethanes

70. As has already been mentioned, the CFMs persist in the troposphere for very long periods of time (about 40 years is the mean residence time for $CFCl_3$ and 70 years for CF_2Cl_2), and the observed buildup of the CFMs in the lower atmosphere suggests that virtually all of the gas released to date is still in the troposphere. There are probably small sinks at the surface and in the troposphere, and there is a long-term sink in the stratosphere, since those molecules that diffuse upward into

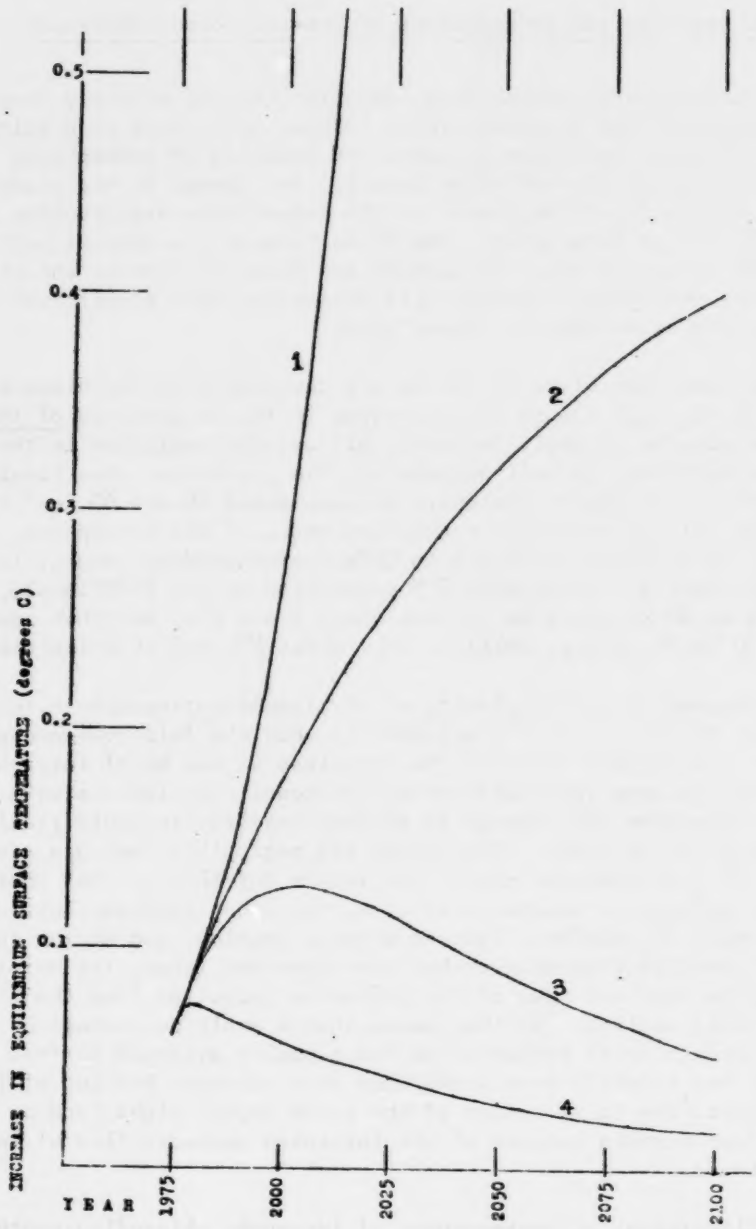

FIGURE 12

Computed equilibrium surface temperature increase due to chlorofluoromethanes in the atmosphere according to various scenarios. (After J.M. Mitchell Jr.)

Curve 1 - at 1975 emission rate until 1979, thence annual five per cent growth
Curve 2 - at 1975 emission rate throughout
Curve 3 - at 1975 emission rate intil 1979, thence annual five per cent reduction
Curve 4 - at 1975 emission rate until 1979, thence total cessation of emissions

the stratosphere are broken down by the ultraviolet radiation there and enter into chains of reactions with other stratospheric components.

71. The present mean tropospheric concentration of total CFMs is about 0.4 parts per billion (10^{-9}) by volume (ppbv), and calculations by Crutzen and others indicate that, if CFMs continue to be produced at the 1973 production rates, by 2000 AD the $CFCl_3$ would reach about 0.32 ppbv and the CF_2Cl_2 about 0.58 ppbv and would level off in the middle of the next century at about 0.7 and 1.9 ppbv, respectively (for example, see NAS report, 1976).

72. The molecules CF_2Cl_2 and $CFCl_3$ have strong infra-red absorption bands in the spectral region 8-12 μm and hence these CFMs absorb and emit radiation in this spectral region where the atmosphere is relatively transparent (more than 75% of the radiation emitted by the surface in this spectral region escapes to space, which for this reason is referred to as the "atmospheric window"). Therefore the atmospheric and surface temperatures are most sensitive to gases that have bands in the 8-12 μm region. The CFMs in the atmosphere would absorb radiation coming from the Earth's surface and emit at the atmospheric temperature, and since, on average, the surface is much warmer than the atmosphere, the CFMs would absorb more radiation energy than they emit. In other words, the CFM infra-red bands would cause a net reduction in the radiative energy emitted to space by the Earth/atmosphere system, which implies that more of the infra-red radiation is retained within the system due to the presence of the CFMs. This enhancement in the amount of radiation retained within the Earth/atmosphere system might tend to increase global surface temperatures. Adopting a simple one-dimensional model of the Earth/atmosphere system, Ramanathan (1975) indicated that the global surface temperature might increase by about 0.9°K (an increase which may be climatically significant) if the tropospheric concentrations of CF_2Cl_2 and $CFCl_3$ were each to increase to 2 ppbv from an assumed level of about 0.1 ppbv. Further, his analysis also suggests that for small changes the increase in the surface temperature is linearly related to the concentration of CFMs.

73. In Figure 12 calculated equilibrium surface temperature changes are shown for a few different scenarios of CFM release. If the worldwide emission rate of CFMs continues to increase by about 5% per year (or half the rate of increase up to the present time), then the temperature rise would be about 1°C by the year 2025. A continued increase of emissions by 10% would bring this date forward to 2010. The calculations may be assumed to be correct to better than a factor of 2.

74. The warming effect of CFMs is similar to the well-known warming effect that an increase in the atmospheric CO_2 concentration may have on the global climate. It should be pointed out that the potential warming effects of increased CO_2 and increased CFMs occur in different spectral regions. A 5% growth rate per year in the release of CFMs would contribute additional warming which would be of the same range as the projected warming effect due to accumulating CO_2 in the atmosphere (about 1.4°C by 2030).

75. It should be noted at this point that the above estimates of warming refer to a global mean temperature, and that the actual patterns of change will be greatly influenced by inevitable changes in the atmospheric circulation patterns. Thus, it is likely that considerably larger changes in temperature will occur in polar regions where there are factors which tend to amplify a temperature change, with relatively

less changes at low latitudes. Regional details cannot be predicted at this time. On the other hand, the precipitation patterns in the sub-tropics may be altered considerably, benefitting some areas and depriving others. Again, it is at present impossible to predict exactly how these patterns of change will appear.

76. Most of the estimates of climate change due to mankind's activities are based on one-dimensional models of the climate system, and there is a need to take better account of the dynamical interactions within the atmosphere and between the atmosphere, the oceans, the ice masses of the polar regions, and the biosphere. Thus, the development of more complete models of the complex system that determines the global climate must be developed before we shall be in a position to give satisfactory and detailed answers to the many problems being raised.

77. Advances in our knowledge of climate mechanisms over the next two years will improve our assessment of both climatic effects due to CFMs (through ozone reduction and displacement and through infra-red absorption), but these advances cannot be expected to make our assessment of the climatic effects as precise as our assessment of ozone reduction. If the increased infra-red absorption and emission due to the presence of CFMs in the atmosphere were to alter our climate by small amounts, the most important effects would be on agriculture, particularly through the boundaries of the regions in which particular crops can be grown effectively, although other agricultural effects are possible.

Biological effects

78. A reduction in the ozone column would result in an increase of UV-B (290 to 320 nm) radiation received at the Earth's surface, and theoretical calculations using both absorption and scattering by ozone and other atmospheric constituents have indicated an average magnification factor from slightly less than 1.5 to slightly more than 2.0 between percentage changes in the ozone column and percentage changes in UV-B radiation in clear sky conditions. In other words, a reduction of 10% in ozone would result in an increase of about 20% in UV-B.

79. However, an important point to note is that whereas an ozone depletion would result in increased penetration of UV-B, in respect of the damaging potential the corresponding increase is even greater than the increase in total UV-B, because the increase is proportionally greater at shorter wavelengths. Relative effectiveness of one quantum for altering DNA (the material carrying the genetic information of all living cells) is roughly as follows:

320 nm	0.03
315 nm	0.1
310 nm	0.6
305 nm	2.6
300 nm	15
295 nm	60
290 nm	160

(these define the action spectrum of UV-B radiation for DNA, which is here normalized to a value of 1000 at 265 nm, the wavelength for peak sensitivity. At still shorter wavelengths the sensitivity drops off.)

80. Whereas the problem of the biological consequences of increased solar UV radiation reaching the Earth's surface is not within the sphere of WMO, the fact that occurrences of sunburn, cancer and eye damage are directly related to the intensity of UV radiation, and the possibility that an increase in UV may also reduce agricultural yields and disturb ecosystems, means that it is essential that the competent bodies undertake appropriate studies. It should be the role of WMO to ensure that the relevant data and information obtained through the Global Ozone Research and Monitoring Project are readily available for these studies.

81. It is assumed that a detailed discussion on the biological effects of ozone depletion will be submitted to the UNEP meeting in Washington, D.C. Nevertheless, the following actions are suggested as being suitable for an interdisciplinary effort in support of studies into the effects on the biosphere of an increase in solar UV radiation:

(a) To document the world climatology (including trends) of the ultraviolet radiation received at the surface of the Earth, particularly in the "active" wavebands for effects on man and the biosphere;

(b) To determine more precisely than is presently known, the "active" wavebands causing effects on plants and micro-organisms;

(c) To determine quantitatively the dose-response relationships for various exposure times;

(d) To develop epidemiological relationships from the information in (a) and (c), the ultimate objective being to provide alternative management strategies.

82. In view of the complexity of the problems involved in these fields, but bearing in mind the seriousness of the possible consequences of an attenuation of the ozone layer, it is proposed that UNEP consider establishing a scientific committee or working group on which the following bodies might be represented:

Governmental: FAO, UNEP, UNESCO (MAB), WHO and WMO

Non-governmental: ICSU and following affiliated unions: UBS, IUGG, IUPAB, IUPS.

83. The purpose of the committee would be to recommend a suitable study programme to investigate the impact on the biosphere of any ozone changes established under the WMO Global Ozone Research and Monitoring Project. It is to be expected that the appropriate UN specialized agencies would accept responsibility for developing programmes within their respective spheres of competence.

IV. MODELLING THE ATMOSPHERIC OZONE PROCESSES

84. In order to make reliable estimates of future changes in ozone amount, it is necessary to rely upon the ability to simulate the physical and photochemical processes in the atmosphere. As the full complexity of the atmospheric processes

cannot be simulated on a laboratory scale, the most efficient tool available is numerical simulation, or modelling, of such processes with the aid of fast electronic computers. It is important to design models of the atmosphere that, on an average basis, simulate or describe the photochemical or physical processes taking place on all scales. Since many models already exist which simulate the atmosphere dynamical-photochemical system in varying degrees of complexity, special effort needs to be made to co-ordinate studies using these models and to establish standard cases and comparative model runs.

One-dimensional models

85. These models maximize the photochemical complexity and representation while requiring that all other atmospheric processes be represented by simple diffusion. They are essential means of determining the importance of the many chemical reactions with their variability in the vertical dimension, and of deriving efficient parameterization schemes for more complex atmospheric models. The major task is to derive a set of diffusion coefficients that are applicable to the problem under study. Efforts must continue to obtain the most reliable eddy exchange coefficients for those models using only diffusive transport (1-D and some 2-D models). A plausible approach would be through studies based on available data of the transport of relatively stable tracers, when assumptions about chemical reactions in the stratosphere would be unnecessary. Special adaptation of these models is required to support the design, intercomparison and interpretation needs of experimental programmes.

Intermediate models

86. Two-dimensional models (latitude, vertical) can represent the major north-south variations in the atmosphere whilst retaining complete interaction between the various photochemical components and the atmospheric circulation. They must, however, represent the synoptic- and planetary-scale waves in the atmosphere by some form of diffusion parameterization, and as yet there is no completely satisfactory formulation of this for all levels. Tests of the models on the ozone/NO_x problems suggest that they give fairly reliable results and a reasonable description of the north-south variations. Development work on parameterization in such models should be encouraged. Since the ozone formation, destruction and distribution processes, as well as those of the associated trace constituents, are highly latitude-dependent, it follows that these models have an important role to play in simulation problems and in interpreting experimental data. More research work needs to be done to develop simplified models which can include the major planetary forcing functions without requiring the full complexity of the three-dimensional general circulation models.

87. In so doing, it should continually be recognized that in these models a major uncertainty results from the necessity of predicting the transport by eddies in terms of zonal mean (longitude-independent) quantities using the diffusion assumption that all net local eddy transfers occur in a downgradient fashion and with a magnitude determined by appropriately chosen exchange coefficients. This assumption is often violated in nature because the meridional circulations and eddies are a tightly coupled pair of processes. In a two-dimensional sense the transport by eddies of heat and quasi-conservative trace constituents can, in general, be considered as acting downgradient, though the one-dimensional (vertical or meridional) components may be countergradient. It is understood that some 2-D models incorporating both diffusion and organized circulation are being developed.

Three-dimensional models

88. Because only the three-dimensional numerical models can adequately represent the synoptic-scale wind systems which are responsible for much of the transport in the atmosphere, and the planetary-scale systems which dominate the winter stratospheric flow, it is essential that they be used to determine and verify many aspects of the ozone problem. As a minimum these models should include complete interaction between the atmosphere's thermodynamics and ozone, as well as the action of other specified trace constituents on ozone. The three-dimensional models should then be used to establish and verify the transport parameterization in simpler models and to test depletion mechanisms wherein the major concentrations determined by similar models are perturbed by variations in an input parameter. Special attention should thus be given to models which can be run in simpler modes or in conjunction with simpler models. It should be understood that even in these complex 3-D models it is assumed that there would be no changes in the way the stratosphere transports trace substances in the event of large ozone reductions due to CFMs; a reasonable assumption since it is not currently known precisely what the response of the atmosphere would be in such circumstances.

Specialized models

89. In addition to regular modelling activities, particular treatment is required for selected parts of the atmospheric ozone problem:

- Many sub-sets of the atmospheric chemistry problem must be handled by the elimination of very short-lived or transient species. Also reactions which vary rapidly at particular times (e.g. at sunrise or sunset) must usually be modelled using slower averaged rates.

- There are specific problems of strongly interdisciplinary nature which must be resolved. Of prime importance in the ozone problem is an improved model for the complete nitrogen cycle, its possible changes due to man's activities and the implications for atmospheric chemistry.

- As regards the climate aspects, studies aimed at assessing the long-term impact of ozone changes on climate should be undertaken, even using highly parameterized models based on currently accepted hypotheses, which should take account of the progress achieved so far in this field.

V. NEED FOR CO-ORDINATED MONITORING PROGRAMMES OF OZONE AND OF RELEVANT TRACE GASES AND ATMOSPHERIC PARAMETERS

90. From the foregoing discussion it should be apparent that research is now urgently needed in order to advance knowledge in the field of atmospheric ozone (including the impact of changes in the amount of ozone). This work could not be successfully undertaken on the basis of the present observing network, and there is

a need for a limited period of intensive observations of ozone (particularly its vertical distribution) and also of those other atmospheric trace gases which have a direct or indirect influence on ozone. A real effort is needed over a period of at least 3-4 years in order to permit many of the assumptions and working hypotheses used in current ozone studies to be confirmed and refined so that future research would be built on solid foundations.

91. The WMO Commission for Atmospheric Sciences Working Group on Stratospheric and Mesospheric Problems has stressed that the generally wide spacing of the observing network and the nature of the parameters to be monitored means that nothing less than global integration would be required, and that it is essential therefore that data from the network be uniform and of very high quality and that they be made widely available. It is hoped that mutual collaboration and assistance between Members in respect of the ozone investigation would be forthcoming in a spirit of international co-operation. Following the initial period of intensive efforts, requirements could be relaxed to a level commensurate with a continuing system of monitoring ozone and other relevant constituents whose main objective would be to detect trends in the global ozone concentration and contribute to better understanding of the stratospheric environment.

92. Monitoring is the process of repetitive measurement, for defined purposes, of one or more elements or indicators of the environment according to prearranged schedules in space and time. There are a number of reasons why it is important to operate a global ozone monitoring system:

(a) To define the ozone climatology of the stratosphere in sufficient detail to determine hemispheric and world trends;

(b) To provide data for research and help in making predictions of future states;

(c) To provide, on a synoptic basis, "ground truth" for many of the critical experiments.

93. A programme of ozone measurements would have limited value in future research without a parallel programme to measure the concentration in the atmosphere of those substances responsible for the destruction of ozone. The most important "parent" substances of the reactive radicals are nitrous oxide (N_2O) and the chlorofluoromethanes (CFMs). They should preferably be monitored both near the ground and in the stratosphere. Since these substances are relatively inert and fairly uniformly distributed in the troposphere, apart from experimental stratospheric profiles of their vertical distribution to define diffusive and decay properties, and occasionally to construct meridional profiles, it would be sufficient if these substances were measured at the baseline air pollution stations to establish trends. Thus relevant geophysical and chemical parameters should be monitored for the following reasons:

(a) To assist in explaining the observed ozone distribution and trends, and to provide essential data for relevant studies;

(b) To document the climatology (including trends) of the ultraviolet radiation received at the surface of the Earth, particularly in those wavelengths causing sunburn.

Scientific design criteria

94. A number of scientific criteria should be followed when recommending modifications and additions to existing systems for monitoring ozone and related geophysical/chemical parameters:

(a) Optimization of network densities requires a knowledge of:

- the variability in time and space of the elements being sampled;
- a conceptual model of the relevant physical-chemical processes;
- the objectives of the monitoring system;

(b) Notwithstanding (a) above, a monitoring network should not be tied too closely to a particular model of the atmosphere. A new model may arise later, and data sets may be used for entirely different purposes than originally contemplated. Thus if some additional measurements can be made at relatively small supplementary cost, then this should be done;

(c) The design of a monitoring system often requires a pilot field study over a limited period of time. It is important that such a study be identified and carried out before the monitoring system becomes operational.

Existing monitoring programmes

The WMO world ozone network

95. The existing network of stations provides the following data:

(a) Total amounts of ozone on particular days and hours at about 80 locations;

(b) Umkehr observations, yielding estimates of vertical distribution of ozone at about 15 of the stations mentioned in (a) but only sporadically taken;

(c) Ozonesonde observations at 5-10 stations, once weekly at the most;

(d) Rocket-borne vertical ozone measurements at one station less than once a month.

The existing network contains gaps, particularly over the oceans and in the Southern Hemisphere, and it is difficult, if not impossible, to separate regional trends (due to shifts in the positions of the long-wave troughs) from global trends in ozone concentrations. The Umkehr technique permits the vertical distribution of ozone to be estimated in a crude fashion using the Dobson spectrophotometer, and knowledge of the ozone variation at heights exceeding 30 km is particularly valuable since CFMs dissociate in this region and should preferentially attack the ozone there.

Satellite measurements of ozone

96. Observations of ozone by a polar-orbiting satellite have the obvious advantages of quasi-global coverage by one and the same instrument (so that observations are readily comparable) and availability of the data in quasi-real time. Moreover, if individual total ozone observational errors using the BUV instrument are random and of an order of 5%, then the hemispheric and global mean monthly ozone content can be estimated to within a fraction of 1%. (Much of this uncertainty is due to the fact that observations in polar latitudes during the winter season are not obtainable at present).

97. The BUV and LRIR type instruments can obtain layer-average ozone amounts at heights above the level of ozone maximum more precisely than any other methods currently available, and thus should be capable of early detection of any reduction of ozone due to photodissociation of CFMs at 30 to 40 km, especially in the tropics.

98. However, the limitations of satellite monitoring systems must also be recognized. The time between the proposal and launch is long (7 years or more), so that such systems are somewhat inflexible for quick turnaround programmes. They are also limited in vertical and horizontal resolution, and often in accuracy, making them in general not very suitable for studies of detailed chemical mechanisms.

99. The following satellite observations of relevant atmosphere parameters have been made so far:

Nimbus 4:	Temperature to 50 km (SIRS, IRIS, SCR) Ozone total, 30-50 km (BUV, IRIS)
Nimbus 5:	Temperature to 50 km (SCR)
Nimbus 6:	Temperature to 80 km (LRIR, PMR) Ozone 15-50 km (LRIR) Water vapour 15-45 km (LRIR)
Atmospheric Explorer E:	Ozone total 30-50 km (BUV)

100. The following are planned for the future:

Block 5D-1 System (1977)	Total ozone, vertical temperature and moisture profiles
Nimbus-G (4th Quarter 1978):	
	Temperature up to 80 km (LIMS, PMR) Ozone 10-50 km (LIMS, SBUV) H_2O, NO_2, HNO_3 (LIMS) H_2O, CO, NO, CH_4, N_2O (SAMS) Aerosols (SAM II)
SAGE:	Aerosols Ozone

Shuttle (after 1980): A large number of active and passive instruments for remote probing of the upper atmosphere are planned for various shuttle missions. The AMPS payload has a portion dedicated to study of the atmosphere from the troposphere to 120 km.

101. The backscatter ultraviolet (BUV) instrument on polar-orbiting Nimbus 4 is still in operation after 6 years, although a power shortage now allows it to operate rather less than half the time. This instrument provides an estimate of total ozone, as well as estimates of ozone amounts in layers above the ozone maximum. The data from Nimbus 4 are being re-reduced because of uncertainties in satellite positioning and orientation, and it is not expected that the data reduction will be completed until early in 1978. Data are available only for those parts of the Earth's atmosphere in sunlight; there is no information from polar winter regions.

102. The Limb Radiance Infra-Red Radiometer (LRIR) on Nimbus 6 (launched June 1975) had a lifetime of six months due to the use of cryogenic cooling. This instrument provides a more detailed picture of ozone variation with height than the BUV instrument, but its ability to assess total ozone is uncertain and may be less accurate.

103. The Atmospheric Explorer E (AE/E) was launched in December 1975 into a low-inclination orbit (± 20° of Equator) and provides BUV ozone data in the tropics. This satellite permits a recalibration of the Nimbus 4 BUV instrument.

104. The polar-orbiting Nimbus G, scheduled for launch in late 1978, will have a two mode step-scanning BUV instrument (SBUV) and a Continuous Scan Mode which will scan the Earth across the orbital track and provide nearly complete areal coverage of the globe each day. Nimbus G will also include an instrument similar to the LRIR (the LIMS).

105. Consideration is being given to incorporating either the BUV or SBUV ozone-measuring instrument into the Tiros N operational satellite series. However, incorporation would probably not take place until the third or fourth member of the series.

The World Weather Watch

106. This is the system organized by WMO to provide synoptic information on the three-dimensional structure of the atmosphere. It is the largest and most reliable environmental monitoring system in the world.

The WMO Background Air Pollution Station Network

107. This network includes 110 identified regional air pollution stations proposed by 65 countries, and about 15 baseline air pollution stations proposed by 9 countries. About half of these are already functioning. An Operations Manual for Sampling and Analysis Techniques for Chemical Constituents in Air and Precipitation has been published (WMO No. 299, 1974).

108. As indicated in paragraph 1.5 of Part II of the Operations Manual, the minimum programme for baseline stations "shall include measurements of CO_2 in addition to turbidity, radiation and chemical composition of precipitation. Measurements of total ozone would also be highly desirable unless they are already being made at a nearby site". Baseline stations and regional stations with expanded programmes are encouraged to monitor other trace gases, and the Operations Manual contains recommended methods for sampling ozone, SO_2, CO, NH_3, NO, NO_2 and N_2O.

109. Baseline stations are fully or partially operational at Mauna Loa (Hawaii), South Pole (Antarctica), Point Barrow (Alaska), Samoa, Ocean Weather Station "Papa" (50°N, 145°W), Alert (Canada), Sable Island (Canada), Mount Hobart (Australia), Patagonia (Argentina), Huancayo (Peru), Minamitorishima (Japan), Kislovodosk (USSR). In addition, financial support has been secured to undertake a site-selection survey of Mount Kenya. Ocean Weather Station "Papa" may have a limited lifetime.

The UV Monitoring Network

110. Dr. D.F. Robertson of Australia has designed a simple instrument which measures global ultraviolet solar radiation with a response function similar to that of human skin sunburning. About half a dozen of these instruments have been operated in and around Australia during recent years. The U.S.A. has installed modified versions of this instrument (the Robertson-Berger Sunburning UV Meter) at some 17 locations within its own country and similar instruments also are used at Davos (Switzerland), Warsaw (Poland) and Aspendale and Brisbane (Australia).

VI. RECOMMENDATIONS

Global ozone monitoring system

111. It is recommended that because global monitoring systems are costly, they should meet the needs of multiple users wherever possible. Thus the world ozone network should be fully co-ordinated with, and sometimes integrated with, the observing systems of the World Weather Watch, the WMO background air pollution network, and the UV monitoring network.

112. An intensive effort should be carried out over a period of 3-4 years with the understanding that following this initial period of intensive effort, requirements could be relaxed to a level commensurate with a continuing monitoring system of ozone whose main objective would be to detect trends in the global ozone concentration.

113. Every effort should be made to ensure that global ozone data are uniform, of high quality, and will be made widely available, and that mutual collaboration and assistance between Members in respect of the ozone investigation is carried out in a spirit of international co-operation.

114. Detailed recommendations for improving the global ozone monitoring system follow in paragraphs 115-143.

Total ozone - ground-based systems

115. In spite of the complexity, the bulk and the expense of the Dobson ozone spectrophotometer, it is recommended that a campaign be launched to bring back into operation as many of the existing Dobson instruments as possible, and to transfer some of these to countries in areas lacking any ground-based means of measuring total ozone. One or two countries, preferably the U.S.A. and Canada, with the necessary facilities for overhauling and recalibrating Dobson ozone spectrophotometers have already accepted some commitments in this respect. An intercomparison and intercalibration test between Dobson instruments will be carried out at Boulder (U.S.A.) in 1977.

116. Urgent attention should be given to the development of new surface-based instruments with the capability of automatically measuring total ozone, and that the forthcoming comparison between the new Canadian (Brewer) instrument and the Dobson be carried out for at least a year, with the hope that a similar comparison can be carried out soon with the New Zealand (Mathews) total ozone instrument. Consideration should also be given to automating Umkehr measurements, including a computer programme to unscramble observations when clouds are present.

117. All the existing, and reactivated, total ozone measuring stations should be maintained for at least 20 to 25 years, and arrangements should be made for a qualified expert on ozone instruments to visit the stations periodically to advise on observing procedure and instrument maintenance and possibly to effect intercomparisons with a travelling standard instrument. This would be additional to systematically conducted intercomparisons between key regional instruments to ensure stability of the quality of collected data. (For further details see paragraphs 133-142).

118. In view of a recent suggestion that near 300 nm the radiation may change by as much as 20% during the 11-year sunspot cycle, whereas it is implicit in the Dobson measurements that this radiation be constant, extraterrestrial ultraviolet (UV) radiation should be monitored as precisely as possible for a few solar cycles (using both an extrapolation to zero air mass of surface UV measurements and direct measurement by satellite).

119. A concensus should be reached concerning the possible influence of atmospheric aerosols on Dobson total ozone measurements, and in particular on the Dobson Umkehr measurements. The problem of the temperature dependence of ozone absorption should also be clarified.

120. A detailed comparison should be made of total ozone estimates obtained by a Dobson instrument under cloudy and clear skies, since there is some evidence that these observations are not completely compatible.

121. Advanced models such as the General Circulation Model at the Geophysical Fluid Dynamics Laboratory (NOAA, U.S.A.) should be used immediately to estimate errors in climatic or hemispheric areal means of total ozone resulting from ozone observations being only at certain Dobson stations, and within certain regions. Comparisons on a daily basis and any trends that may occur should be used for this purpose.

Satellite stations

122. It is recommended that the best available ozone measuring sensors be considered a primary requisite among satellite instrumentation.

123. Member countries operating meteorological satellites should be encouraged to include atmospheric ozone sensors of proven capability aboard future satellites, with the hope that continuous ozone measurements by satellite can be obtained for at least one solar cycle (11 years).

124. Efforts should be made to ensure that the BUV data become available to the user within one year of the observations.

125. The BUV data should periodically be compared with high quality data from Dobson ozone spectrophotometers and balloon-borne ozonesondes. Moreover, data from rocket-borne ozonesondes should be improved to a degree at which they may be used also for intercomparison with satellite-borne sensors.

126. Efforts should continue to develop limb-radiance instruments capable of observations for several years (these instruments can measure ozone profiles better than the BUV instrument and to lower altitudes, but the total ozone amount derived thereby may not be quite so accurate).

127. As soon as the reduction of the Nimbus 4 total ozone data up to the end of 1976 has been completed, a comparison should be made between the trend (since 1970) determined from these data and from the surface-based Dobson network, thus indicating the error in hemispheric and global ozone trends deduced from the Dobson network.

128. Climatic monitoring of stratospheric temperatures should be carried out in concert with the monitoring of stratospheric ozone so that trends can be compared, since ozone equilibrium values may be partially a function of temperature. (Note: while an attempt is being made in the U.S.A. to determine the worldwide temperature trend in the lower stratosphere from radiosonde data, this is much more logically done from satellite information, particularly at the higher elevations, where radiation effects on radiosonde temperatures are severe).

Umkehr measurements

129. It is recommended that all stations with a Dobson ozone spectrophotometer be urged to make Umkehr measurements as regularly as possible (at least 10 to 15 per month). A relatively large number of observations is necessary in order to offset the rather high uncertainty of single observations using this technique. In this connexion there is a need to study the influence of dust when calculating the results of high-level Umkehr observations. Moreover, there would be great advantage in developing automatic instruments in conjunction with a computer programme to unscramble observations made when clouds are present.

130. As regards the location of stations making Umkehr observations, it is recommended that at a minimum the 12 or so stations already making them continue to do so and that every effort be made to initiate observations at tropical stations where any effect of CFMs on ozone should be manifested the earliest. Possible locations could be Darwin, Huancayo, Mt. Kenya, Mauna Loa, Samoa and Singapore.

Other (extra-tropical) locations where Umkehr observations would be particularly valuable are Boulder, Resolute, South Pole, Toronto and Tromsö.

131. It is recommended that a meeting of experts on Umkehr methods be convened to clarify once and for all the accuracy and usefulness of data obtained by the Umkehr technique, and in particular whether the data are useful only in the absence of satellite measurements or can also serve to supplement satellite measurements. Careful consideration should be given to the influence of atmospheric aerosols on Umkehr measurements, specifically volcanic dust.

132. Finally, in view of the imprecision of the Umkehr method, it is recommended that efforts be continued to develop alternative indirect methods, such as the dye-laser lidar technique and the ground-based BUV technique.

Dobson spectrophotometer total-ozone network stations

133. It is recommended that the following action be taken with respect to stations on or just south of the Equator, where the daily, annual and quasi-biennial variations in total ozone are a minimum, and where any effect of CFMs on these trends should be most noticeable:

- The existing total-ozone station at Huancayo (Peru) be recalibrated as soon as possible (the trend at this station has been under suspicion for years, being upward when other tropical stations were downward);

- The newly-established total-ozone station in Samoa be maintained with great care since it must be representative of the entire equatorial Pacific;

- The total-ozone station at Darwin (Australia) destroyed by a tropical storm be reactivated as soon as possible;

- A total-ozone station be established at Singapore (directly on the Equator) and/or at Manila (Philippines);

- The plans for establishment of a total-ozone station on Mt. Kenya be carried forward, with the hope that some nation might contribute an inactive Dobson ozone spectrophotometer for this station. The proximity of Mt. Kenya and Mahe (Seychelles) would hardly justify a Dobson instrument at both locations, and preference should be given to Mt. Kenya since it is a background air pollution station;

- Every effort be made to establish a total-ozone station in Ghana or Nigeria;

- The total-ozone station located at Rio de Janeiro should be upgraded to make regular observations as soon as possible.

134. Since variations in total ozone amounts in polar regions are almost completely dominated by atmospheric transport processes and hence reflect variations in the atmospheric circulation, and since the most likely technique for ozone measurement by satellite (BUV) will not provide data from these regions during the polar night, it is recommended that moonlight observations be taken wherever possible at high-latitude stations, and in particular that:

- Every effort be made to improve the quality and quantity of the total-ozone data at Amundsen-Scott (South Pole), which for the past 10 years has provided ozone data only during a few summer months;

- The total-ozone station at Halley Bay (U.K. station in Antarctica) be reactivated to provide a back-up to Amundsen-Scott (Halley Bay provided excellent total-ozone data until 10 years ago);

- The total-ozone station at Tromsö be reactivated (this station had a period of record in excess of 30 years, and the cessation of observations there in 1969 was most unfortunate);

- The newly-established total-ozone station at Point Barrow be maintained with care since it must represent much of the western Arctic;

- The existing high quality of observations from Resolute be maintained, this station being especially important because of its proximity to the north magnetic pole (possible influence of solar proton events);

- The station at Spitzbergen be reactivated if feasible, considering the problems of personnel, supply, etc. (The station was previously in operation for only a few years).

135. Recognizing that at present the total-ozone network in southern temperate latitudes is basically an Australian-New Zealand network and that representative hemispheric values of total ozone cannot be obtained from such a station distribution, it is recommended that:

- The total-ozone station at South Georgia continue in operation;

- The station at Puerto Montt (Chile) should be reactivated if possible; if this is not possible the Dobson instrument there (which is the property of the U.S.A.) should be recalibrated and made available for use elsewhere;

- A total-ozone station be established as soon as possible in southern Africa;

- Consideration be given to establishing a total ozone station at Gough Island in the Atlantic Ocean and at Amsterdam Island in the Indian Ocean (Members might wish to provide inactive Dobson instruments for this purpose);

- A new total-ozone station should be established if possible in South America south of about latitude 45°S;

- The total ozone station at Buenos Aires be continued in full operation.

136. Since it has not been possible to integrate total ozone data obtained using filter ozonometers into the north temperate latitude average because, though the sense of the trend is not inconsistent, its magnitude is 4-5 times greater than found in other north temperate regions (e.g. Europe, North America), it is recommended that:

- The ongoing comparison between the filter ozonometer and the U.S.A. Dobson standard at Boulder be carried out for at least a year so that some sort of trend comparison can be made, and that particular attention be given to the influence of atmospheric aerosols on the readings of the filter ozonometer;

- In view of the known differences between the types of instruments, consideration should be given to supplementing the filter ozonometer network with a small number of Dobson instruments which are not in use in other countries.

137. The People's Republic of China represents the largest land area in the Northern Hemisphere without any total-ozone measurements, and the inclusion of China in this type of international scientific effort is highly desirable. It is therefore recommended that:

- At least two Dobson ozone spectrophotometers be sent to China, with the suggestion that at least one of the instruments be placed in the interior of the country. Members might wish to provide inactive Dobson instruments for this purpose.

138. Recognizing the relatively high density of the European total-ozone network leading to a certain redundancy in data, it is suggested that European nations wishing to reduce or eliminate their Dobson ozone spectrophotometer network might be encouraged to offer their instruments through WMO for use in more remote locations.

139. Moreover, it is recommended that:

- The instrument at Val Joyeux (France) be recalibrated, since its total ozone values have been so anomalous that it has not been possible to include this station when computing the European regional average;

- The instrument at Aarhus (Denmark) be recalibrated and an attempt made to find out why the time trend in total ozone at this station is so different from other European stations. If this station is no longer to be considered reliable, thought should be given to reactivating the total-ozone station at Oslo (Norway);

- The stations of Postdam (German Democratic Republic), Hradeč Kralove (Czechoslovakia), Lisbon (Portugal), and Cagliari (Italy) attempt to upgrade their total ozone measurements;

- Attention be drawn to the close proximity of the total ozone stations at Oxford and Bracknell (United Kingdom);

- An investigation be made as to why monthly total-ozone data are often so late in arriving at the World Data Centre in Toronto (Canada) from European stations, and why no data at all are received by the Centre for some months.

140. The North American total-ozone network now seems to be satisfactory following some earlier problems with White Sands, nevertheless it is recommended that the proposed new total-ozone station in southwestern U.S.A. (California, Arizona or Nevada) be established as soon as possible (replacing the station at Green Bay which was too close to Toronto). In addition, consideration should be given to establishing a total-ozone station in northwestern U.S.A. (Washington, Oregon or Idaho).

141. The Japanese total-ozone network of 4 stations appears to be of above-average quality, although 3 of the instruments are copies of Dobson spectrophotometers. The India-Pakistan network now seems to be stable after some erratic early years. It is recommended that stations in the total-ozone networks of Japan and India-Pakistan endeavour to maintain their presently high standards.

142. The subtropics are of considerable interest because of the predominance of the quasi-biennial oscillation in total-ozone there, and it is important to determine the longitudinal variability of this oscillation as well as its relationship to any long-term trends. Therefore it is recommended that:

- The total-ozone station at Cairo (Egypt) continue in full operation;

- The total-ozone station at Casablanca (Morocco) be recalibrated and made fully operational;

- A total-ozone station be established at Manila (Philippines) to replace the station in Taiwan which is no longer reporting (Members might wish to provide an inactive Dobson ozone spectrophometer for Manila); This is a critical meridional link between Japan and Australia;

- The total-ozone station at Mauna Loa (Hawaii) endeavour to continue its high level of performance;

- The total-ozone station at Mexico City be brought into full operation;

- The total-ozone station at Kingston (Jamaica) be reactivated; if this is not possible, the Dobson instrument there might be recalibrated and used elsewhere.

Ozonesonde network

143. There is now a particular need for a reliable 3-dimensional climatology of ozone which does not yet exist to the degree required for theoretical investigations. It is therefore recommended that:

- A network of ozonesonde stations be established as a special programme for a period of 3 to 4 years;

- Prior to starting the programme, an ozonesonde intercomparison test be held since several different types of ozonesondes are available commercially;

- Existing ozonesonde stations with substantial periods of records should be maintained and their observation programme increased to the extent possible;

- Soundings be made at the tropical stations of Cachoeiro Paulista (Brazil), Huancayo, Mauna Loa, Nairobi and Singapore (or Manila) twice a week;

- Soundings be made at the polar stations of Amundsen-Scott, Fairbanks (Alaska), Halley Bay, Heiss Island, Resolute, and Tromsö 3 times a week in winter and spring and twice a week in summer and autumn;

- In south temperate latitudes, soundings be made twice a week at least at Aspendale, South Georgia and at a station in southern Africa, and if possible also at Brisbane, Invercagill, and Macquarie Island;

- In north temperate latitudes the present station network be augmented by soundings at least twice a week at Boulder, Edmonton, Lindenberg, Oslo (or Stockholm), Tateno, New Delhi and Yakutsk; possibly also at Brussels, Cagliari, Fort Churchill, Goose Bay, Tallahassee, Kagoshima, Sapporo, Poona, Trivandrum and Alma Ata;

- A two-week period of daily soundings be attempted in middle and high latitudes of each hemisphere in the early spring of each year.

Measurement of minor atmospheric constituents

144. Many of the reactive or inter-reactive atmospheric trace substances would need to be measured simultaneously through vertical and horizontal traverses with highly sensitive instruments. Instrumental capabilities are developing very rapidly in this area and attention needs to be given to intercomparison, calibration, standardization, development and information exchange.

145. The results of intercomparison tests should be used to identify the most reliable instrumentation for measurement of each constituent, and thereby to assemble optimum packages of instruments to measure the constituents in each reactive group. When possible, the packages for two or more groups should be combined in the same payload to obtain additional insight into the interaction between groups.

146. The station locations and programmes of the WMO Background Air-Pollution Station Network should be reviewed periodically in the light of the potential contributions this network can make towards reaching the objectives of the World Ozone Network, and vice versa.

147. Recommendations for observational requirements in respect of the relevant atmospheric trace constituents are as follows:

(a) Oxides of nitrogen (NO_x) system

N_2O - monitor at baseline stations to an accuracy of 2% twice per month;

- measure dependence on season, latitude and altitude once per season;
- obtain a few high-level vertical profiles.

NO, NO_2, NH_3, HNO_3

- make simultaneous measurements with accuracy of at least 1 ppb (10^{-9});
- carry out intercomparisons of instruments and analysis techniques.

N_2O_5 - develop measuring techniques;

improve laboratory data on NO_2 - N_2O_5 cycles.

Chlorofluoromethanes, N_2O, NO, NO_2 and NH_3 should be monitored once per season in sea water within a few appropriately selected Marsden squares of the world's oceans.

(b) Oxides of hydrogen (HO_x) system

H_2O - determine climatological distribution in the stratosphere;

- continue U.S.A. balloon observations, partly as ground truth for satellites;

HO_2, H_2O_2 - develop measuring techniques;

OH - establish observational methodology and determine latitudinal and vertical distribution.

(c) Chlorofluoromethanes system

Continue U.S.A. programme of stratospheric monitoring of CFMs (at present $CFCl_3$ as well as SF_6) with an attempt being made to obtain measurements once every three months, rather than three times a year as at present. Make ground-based observations at some baseline air pollution stations (at least one in each hemisphere and one in the

tropics) to an accuracy of 5% to monitor global amounts and detect trends (measurements are already being made at Mauna Loa, Point Barrow, Samoa and the South Pole as well as at Adrigole (Ireland) but with hardly this degree of accuracy). Every effort should be made to upgrade the quality of the CFM measurement at the surface since difficulties have been experienced in this regard at all the above stations (the best estimate is that at Adrigole where "clean air" values of $CFCl_3$ increased from about 110 to about 150 ppt (10^{-12}) between 1974 and 1976). It is very important in this regard that truly "clean air" values are obtained, and at least in the case of Adrigole this requires the determination of hindcast trajectories for a period of at least a week, to ensure that the air has come across the Atlantic and not from Europe. In addition the following observations are recommended:

HCl - obtain vertical profiles through the troposphere and the stratosphere in at least three different latitudes in each hemisphere once per season;

ClO_x - continue development of stratospheric measuring techniques and analysis;

CF_2O, CFClO, $ClNO_3$
- attempt to identify and measure;

(Cl, Br)
- initiate research efforts on bromine and on other chlorine components.

(d) Other relevant system

CH_4, CO, H_2 - monitor at baseline stations to an accuracy of 1% ;

- obtain vertical profiles through the troposphere and the stratosphere at different latitudes.

148. In some cases full measurements may not yet be possible. Every effort should, however, be made to obtain the vertical distribution of OH with about the same number of experiments as made for measuring the other substances.

149. This special effort should be based on presently developing national programmes which should be co-ordinated. As a first step, a thorough programme of intercomparisons of different measurement techniques is needed, and further development carried out where necessary. This intercomparison programme should lead to defined experimental packages being used in a co-ordinated observational campaign during subsequent years. This campaign should consist of co-ordinated flights of multiple experiment payloads at the same location in order to obtain complementary measurement sets, as well as latitudes, including the tropics and polar regions, with several experiments per season. In the case of some semi-stable species where latitudinal cross-sections may be obtained by the use of aircraft, measurements should also be extended into the Southern Hemisphere.

150. As in the case of ozone soundings, not only must rapid data evaluation be carried out, but also a centralized scrutiny which will permit changes in the operational scheme to be recommended for the second year on the basis of the results obtained during the first.

The UV Monitoring Network

151. It is recommended that the appropriate WMO bodies (CAS and CIMO) be asked to undertake assessments of methods for monitoring ultraviolet radiation. The initiative of Australia and the U.S.A. in this field is appreciated, and high priority should be given to making an assessment of the Robertson-Berger UV meter.

152. In order to detect variations and trends in UV, and to correlate these with the ozone data, the following measurements are needed:

At ground level - determine UV flux as a function of ozone, haze, clouds and surface albedo, preferably with spectral resolution, in various latitude bands at least once per week.

From satellites - obtain measurements of UV flux in the band 1800-3200 Å to an accuracy of 2 to 3 percent with a 25 Å spectral band resolution.

Studies of photochemistry

153. There are various fields in which research is needed in order to arrive at a fuller understanding of the stratospheric photochemical processes, of the transport mechanisms and of the role played by ozone in the radiation budget. Most of the relevant fields form part of a complex system with mutual feed-back; thus the main goal should be the investigation of all such inter-relationships, in conjunction with the development of a three-dimensional model which incorporates full ozone photochemistry.

154. It is necessary to conduct certain experiments in the laboratory in order:

(a) to provide the relevant atmospheric chemical rate constants for significant reactions in the atmosphere as input to models;

(b) to provide photodissociation, photoionization and absorption data on the relevant molecular and atomic species occurring in the atmosphere as input data for models;

(c) to provide spectroscopic data on molecular and atomic species for the interpretation of experimental measurements;

(d) to carry out a critical survey and evaluation of existing experimental data on the above and recommend standard values for use in model calculations.

155. It is recommended that work in the following fields of atmospheric chemistry be intensified or initiated:

(a) The nitrogen system, including the nitrogen cycle and various multidisciplinary aspects including fluxes of N_2O over different surfaces (forests, oceans, etc.). In particular, whether N_2O is predominantly from the land or the sea (to throw light on the significance of the fertilizer problem), the effect of increasing acidity of precipitation (due to anthropogenic effects) on the percentage of N_2O and N_2 released in denitrification, and the question of a tropospheric sink for N_2O. Furthermore, attention should be given to the rate constant for the reaction $O^* + N_2O$, since this has recently been suggested to be much lower than values used in current models (other reactions involving O^* should also be examined more closely).

(b) The hydrogen system, including the rate constants for reactions involving OH and the chlorofluoromethanes, and extending present measurements to cover pressure and temperature ranges relevant to atmospheric processes. In addition, the rate for the reaction $OH + HO_2$ and all other reactions involving HO_2 (especially $Cl + HO_2$) which have a role in the destruction of ozone should be studied, and maps of measured OH, HO_2 prepared.

(c) The chlorine system, including the rate constants for reactions involving the higher order oxides of Cl, in particular $ClO + O_3 \longrightarrow ClO_2 + O_2$. The photodissociation rates for ClO_2 and ClO are also needed to estimate the amount of ClO_2 in the atmosphere. In addition more study is needed on the rate constant for $Cl + CH_4$, which has recently been claimed to be slower than previously thought, thus allowing more time for chlorine in the catalytic cycle, and on the ratio ClO/HCl which has recently been claimed to be higher than previously thought, suggesting a greater efficiency for the ClO catalytic chain.

(d) The whole problem of the stability of chlorine nitrate and its expected effect in reducing the catalytic destruction of ozone by chlorine and nitrogen oxides.

(e) Study of the night-time photochemical processes, and ways of measuring relevant trace substances at night.

(f) Study of heterogeneous reactions in the troposphere, in particular the washout of NO_x, HNO_3, HCl and H_2O_2.

(g) Improvement of spectroscopic measurements to permit remote sensing of several stratospheric trace constituents, for example: the absorption cross-section of HNO_3 in the 11μ band should be extended to low temperatures; infra-red spectroscopic data for N_2O_5 and HO_2; line strengths for many molecules, including HCl, in the sub-millimetre region.

(h) Examination of the extent to which methyl chloride (CH_3Cl), methyl bromide (CH_3Br) and carbon tetrachloride (CCl_4) are anthropogenic or natural, thus clarifying the problem of the "natural reservoir" of chlorine in the stratosphere. Affirm that there are not large natural sources of chlorine presently in the stratosphere.

(i) Data on the extraterrestrial solar spectrum are available, but more information on the variation of the UV fluxes between solar maximum and minimum would make it possible to separate long-term natural and anthropogenic variations in ozone.

(j) Absorption by O_2 and O_3 and multiple molecular scattering should be included in theoretical ozone calculations.

(k) In addition to solar fluxes, the rate constants for photodissociation of atmospheric gases depend upon the absorption coefficients and quantum yields at different wavelengths. While the gases of primary importance in stratospheric ozone chemistry have been extensively studied, there is a lack of information about others, e.g. H_2O_2.

(l) A closer study of the local production of ozone in the troposphere as a result of intense industrial pollution is important in view of the importance to the global ozone budget.

Analysis and circulation studies

156. In the WMO Global Ozone Research and Monitoring Project it is recognized as essential that regular hemispheric and global analyses of the basic dynamic and thermodynamic variables (ω, P/φ, T) in the stratosphere, and of total ozone and the ozone mixing ratio be maintained and be available to the scientific community. Such analyses are necessary to properly identify hemispheric or global trends in thermodynamic parameters and in total ozone to serve as the basis for comparative studies on special experiments or special events, and also as the framework for considering the representativeness of observations on other trace constituents.

157. Regular analyses up to 10 mb and analyses of total ozone distribution should be on a daily basis; analyses for higher levels and analyses of ozone mixing ratio and other parameters should be made at least weekly in the summer hemisphere and every two or three days in the winter hemisphere. In general these analyses need to be carried out where required global observational data including satellite data are available, as well as objective analysis procedures.

158. Special studies of the circulation and energetics of the stratosphere are to be encouraged. In view of the incompleteness of the observational data at these levels, the studies should be combined with theoretical or numerical studies or special observational programmes. In particular the magnitude and vertical extent of the Hadley Cell and the whole question of the rapidity with which trace gases released at the Earth's surface may reach the 30 km level needs to be investigated (this problem is basic because it indicates how much of the ozone reduction due to CFMs could be expected to be observed now).

159. The co-ordinating body for the project should ensure that such studies are undertaken in connexion with specified intensive observational and experimental periods.

160. In accordance with the above, every effort should be made to improve the reality of atmospheric models, including realistic values of mean meridional circulation (not just an alteration of the eddy diffusivity values to include the effect of mean meridional circulations).

Studies of special events

161. Since the disturbance of the "normal" ozone balance by natural or man-made events is of major concern it follows that special events of large magnitude will provide unique opportunities to study the underlying processes. Efforts should be made to co-ordinate information exchange, intensify ozone measurements, and promote special investigations of stratospheric warmings, volcanic eruptions, solar events and unusual man-made emissions.

Ozone modelling

162. Since many models already exist which simulate the atmospheric dynamical-photochemical system in varying degrees of complexity, special efforts need to be made to co-ordinate studies using these models and to establish standard cases and comparative model runs.

163. It is suggested that efforts be made to obtain the most reliable eddy exchange coefficients for 1-D and 2-D models. A possible approach could be through studies based on data available on the transport of relatively stable tracers.

Source inventories

164. Not entirely unrelated to the topic of monitoring is the question of an inventory of sources of CFMs, nitrogen oxides and other substances relevant to stratospheric ozone. In order to explain trends in ozone concentration and to prepare scenarios for the future, there is the need to keep track of the annual releases of relevant trace gases into the atmosphere, from both man-made and natural sources. Although the estimates must often be inferred indirectly, e.g., from manufacturers' production records or from gasoline sales, these data are a valuable input to photochemistry models.

165. It is therefore recommended that UNEP be asked to obtain from the appropriate bodies annual global inventories for:

(a) chlorofluoromethane production and use;

(b) nitrogen fertilizer production and use;

(c) stratospheric aircraft emissions;

(d) volcanic eruptions that penetrate into the stratosphere;

(e) other factors that may be identified in the future.

Co-ordination of atmospheric studies

166. It is evident that a programme of the scope proposed would entail careful international co-ordination. It is recalled that IUGG in its Resolution XV (6 September 1975) asked WMO in particular to provide encouragement, support and co-ordination to the efforts of all nations in expanding research and monitoring efforts in order to evaluate possible global consequences of any activities which could affect the stratosphere. It was recognized that WMO had considerable experience in co-ordinating Members' activities in such international projects as the programme now proposed, and it is therefore proposed that the focal point be located at the WMO Secretariat.

167. The importance is stressed of putting the data obtained in the observing programme and the research results to use as quickly as possible in compiling statistics, in preparing analyses and in applying them in the various research projects. This means that efficient data management of the proposed international programme, based on the national efforts, is of very great importance. It is noted that it is planned that data obtained from the Nimbus-G satellite (U.S.A.) (see paragraph 100) will be archived and available for use within one year.

168. In support of the various research activities it is proposed that at an international level within the framework of the WMO Global Research and Monitoring Project action be taken to:

(a) Establish an information and co-ordination centre at the WMO Secretariat which will ensure that the necessary ozone research studies and modelling experiments, standardizations and comparisons are carried out and results rapidly exchanged;

(b) Ensure that a global stratospheric analysis programme is maintained. This should include standard mappings of wind and temperature variables, ozone mixing ratio and total ozone and regular N-S cross-sections. Arrangements should also be made for the additional requirements of special observational and experimental periods;

(c) Encourage studies and co-ordinate the meteorological activities associated with investigating special events impacting on the ozone layer;

(d) Organize and sponsor international conferences on subjects relevant to the objective of the Global Ozone Research and Monitoring Project, as well as informal planning meetings on specific problems arising from the implementation of the Project.

Conclusion

169. In conclusion, it is recommended that there should be two types of activity:

(a) An intensive research and monitoring effort (the Global Ozone Research and Monitoring Project) of three to four years' duration, starting during 1977, aimed at resolving current urgent problems and providing the basis for advice to Members and appropriate international organizations;

(b) The laying down of the basis for a continuing research and monitoring programme to cover at least one solar cycle (11 years) in the light of the experience and results of the project above, in order to determine trends.

170. The following major tasks have been identified:

(a) Improve the global monitoring of ozone, and monitor those quasi-permanent trace constituents which impact on the ozone system, as well as the ultra-violet flux;

(b) Co-ordinate national and international experiments aimed at making widely distributed atmospheric measurements, preferably simultaneous, of all pertinent trace constituents;

(c) Ensure efficient data management and analysis;

(d) Encourage and co-ordinate laboratory measurements of the behaviour and reaction rates of the chemical systems at stratospheric temperatures;

(e) Encourage, co-ordinate and assist in studies of the composition of, and the transport and exchange process in the atmosphere, including chemical and photochemical processes; also studies of the influences of cyclic and sporadic events on ozone and on other relevant trace constituents, in connexion with an assessment of the impact on global climate of any changes in the ozone content of the atmosphere;

(f) Support and encourage the frequent exchange of scientific information and personnel, as well as training in relevant fields, the design of better instrumentation, intercomparison tests and international network inspection;

(g) Encourage and facilitate investigations by competent bodies into the impact of UV variations on man and the biosphere.

Implementation of the project

171. Most activities will be nationally sponsored. WMO will take the lead in stimulation and co-ordination of these activities in collaboration with UNEP and ICSU.

APPENDIX A

Resolution adopted by the WMO Executive Committee

Resolution 8 (EC-XXVIII)

GLOBAL OZONE RESEARCH AND MONITORING PROJECT

THE EXECUTIVE COMMITTEE

NOTING:

(1) Resolution 13 (EC-XII),

(2) Resolution 29 (EC-XVIII),

(3) Resolution 10 (EC-XXII),

(4) Abridged report of Cg-VII, general summary, paragraph 3.2.1.3 and 3.3.5.21,

(5) Abridged report of EC-XXVII, general summary, paragraph 3.3.7.2,

COMMENDS the president of CAS for having arranged for the preparation of the text of the WMO statement entitled "Modification of the ozone layer due to human activities and some possible geophysical consequences";

APPROVES the action taken by the Secretary-General in releasing this statement;

CONSIDERING:

(1) The urgent need to determine the extent to which human activities may contribute to the attenuation of the ozone layer due to pollution of the stratosphere, and the need to assess the geophysical consequences of any changes in the ozone content,

(2) That any such study must be conducted in such a way as to ensure that the results will command wide acceptance in the scientific community,

(3) That WMO is the appropriate body to organize such a study,

(4) That the success of the study would largely depend upon Members' own efforts in contributing to a greatly improved global monitoring system of the stratospheric environment,

(5) That there is a need to speed up the publication of data on total ozone amounts,

EXPRESSES APPRECIATION:

(1) To Members which have already taken steps to expand their programme of observations of ozone and other trace constituents in the stratosphere, and have undertaken related research;

(2) To the International Ozone Commission of IAMAP for its valuable collaboration;

(3) To the Atmospheric Environment Service of Canada for providing the services of the World Ozone Data Centre and publishing regularly the bulletin "Ozone data for the world";

APPROVES:

The Global Ozone Research and Monitoring Project as outlined in the annex to this resolution;

URGES Members:

(1) To contribute to the implementation of the project, in particular by establishing, upgrading, re-activating or maintaining ozone observing stations as required to complete the network, bearing in mind the desirability of locating stations near to rawinsonde stations and where feasible in conjunction with background air pollution stations;

(2) To co-operate in a more rapid exchange of data on total ozone amounts by sending their data promptly, if possible monthly, to the World Ozone Data Centre at Toronto for publication;

(3) To make measurements of other atmospheric trace constituents relevant to ozone; and

(4) To contribute to the co-ordinated research efforts outlined in the annex to this resolution;

REQUESTS the president of CAS and other constituent bodies concerned to co-ordinate and intensify their efforts and to provide information on the accuracy of vertical profiles of temperature, humidity and wind speed in the upper atmosphere obtained from satellites;

REQUESTS the Secretary-General:

(1) To proceed, in consultation with the president of CAS, with the planning and execution of the Global Ozone Research and Monitoring Project in accordance with the outline in the annex to this resolution;

(2) To seek continued support from UNEP and other appropriate bodies in the implementation of the project;

(3) To consult with the presidents of technical commissions concerned with a view to using to the fullest extent possible existing groups of WMO technical commissions, especially CAS, in the execution of the project;

(4) To provide the necessary support for the execution of the project within the limits of available financial resources;

(5) To discuss the feasibility of further accelerating the exchange of total ozone data with the presidents of the technical commissions concerned;

(6) To bring this resolution to the attention of all concerned.

Annex: 1

Annex to Resolution 8 (EC-XXVIII)

WMO GLOBAL OZONE RESEARCH AND MONITORING PROJECT

1. The increasing attention given to the various ways in which man may influence the chemical processes in the global atmosphere, particularly the recent concern regarding the effect on ozone of emissions from supersonic aircraft and of chorofluoromethanes, highlights the need for initiating already in 1976 an internationally co-ordinated project to improve our understanding of the complex interactions which determine stratospheric environmental systems.

2. It is now clear that whereas ozone (O_3) is formed by the photodissociation of molecular oxygen, its catalytic destruction by nitrogen oxides (NO_x) is the predominant stratospheric removal mechanism under normal conditions. The major source of nitric oxide (NO) is oxidation in the stratosphere of nitrous oxide (N_2O) originally released by microbiological activity in the soils and oceans.

3. The possibility thus exists that additions to this NO_x source, or the addition of other interactive substances such as chlorofluoromethanes, could seriously disturb the ozone balance. The weight of expert scientific evidence, based on models and on admittedly scant atmospheric measurements, is that future large aviation fleets flying at higher levels may perturb the NO_x levels sufficiently to require controls of their emissions and that the continued release into the atmosphere of man-made chlorofluoromethanes poses an even more serious threat.

4. The distribution of ozone is influenced to a major extent by dynamical processes, and existing data are not sufficient to allow a full understanding of the extent and nature of this interdependence.

5. The foregoing considerations clearly point to the need for a co-ordinated joint international project to find scientifically sound answers to questions concerning the role of anthropogenic pollutants in reducing the quantity of ozone in the stratosphere,

with particular emphasis on chlorofluoromethanes and nitrogen oxides, and on the possible impact of changes in the stratospheric ozone content on climate.

6. It is recognized that WMO must play a leading role in the organization, execution and evaluation of this project, and it is expected that its outcome will be of great significance to Members and to some intergovernmental organizations such as UNEP, since the results of the project may justify calls for measures to limit the production of particular substances, with inherent economic implications.

Objectives

7. The Global Ozone Monitoring and Research Project should enable WMO to provide advice to Members and to the United Nations and other appropriate international organizations concerning:

(a) The extent to which man-made pollutants might be responsible for reducing the quantity of ozone in the stratosphere, with particular emphasis on the role played by chlorofluoromethanes and nitrogen oxides;

(b) The possible impact of changes in the stratospheric content of ozone on climatic trends and on solar ultra-violet radiation at the Earth's surface;

(c) The establishment of the basis and identification of the needs for strengthening the long-term monitoring programme of the ozone system for determination of trends and of future threats to the ozone shield.

Strategy

8. The means by which the objectives may be achieved are as follows:

(a) To gather and evaluate existing knowledge on atmospheric ozone;

(b) To provide information on the atmospheric concentrations of substances of relevance to the N_2O, NO_x, HO_x, ClO_x, BrO_x cycles leading to a better appreciation of their currently known important sources and sinks and their impact on the ozone budget;

(c) To extend and improve analyses and circulation studies of the stratosphere based on actual data, with a view to clarifying and predicting the exchange processes between the troposphere and the stratosphere;

(d) To assess the impact on the atmospheric environment of possible ozone depletion, recognizing that this involves a variety of interdisciplinary interactions requiring input from the fields of meteorology, oceanography, agriculture and microbiology;

(e) To arrange for an exchange of knowledge through reports, newsletters, scientific meetings and exchange of personnel.

Programme of work

9. There should be two types of activity:

(a) Intensive research and monitoring effort (the Global Ozone Research and Monitoring Project) of three to four years' duration, starting during 1976, aimed at resolving current urgent problems and providing the basis for advice to Members and appropriate international organizations;

(b) The laying down of the basis for a continuing research and monitoring programme to cover at least one solar cycle (11 years) in the light of the experience and results of the project above, in order to determine trends.

10. The following major tasks have been identified:

(a) Improve the global monitoring of ozone, and monitor those quasi-permanent trace constituents which impact on the ozone system, as well as the ultra-violet flux;

(b) Co-ordinate national and international experiments aimed at making widely distributed atmospheric measurements, preferably simultaneous, of all pertinent trace constituents;

(c) Ensure efficient data management and analysis;

(d) Encourage and co-ordinate laboratory measurements of the behaviour and reaction rates of the chemical systems at stratospheric temperatures;

(e) Arrange, with other responsible agencies as necessary, for an inventory to be maintained of the annual emissions of chlorofluoromethanes, nitrogen oxides and other important species, as well as of national production rates;

(f) Encourage, co-ordinate and assist in studies of the composition of, and the transport and exchange process in the atmosphere, including chemical and photochemical processes; also studies of the influences of cyclic and sporadic events on ozone and on other relevant trace constituents, in connexion with an assessment of the impact on global climate of any changes in the ozone content of the atmosphere;

(g) Support and encourage the frequent exchange of scientific information and personnel, as well as training in relevant fields, the design of better instrumentation, intercomparison tests and international network inspection;

(h) Encourage and facilitate investigations by competent bodies into the impact of UV variations on man and the biosphere.

Implementation of the project

11. Most activities will be nationally sponsored. WMO will take the lead in co-ordinating these activities in collaboration with UNEP and ICSU.

12. As regards the scientific direction and arrangement of the project, this should be carried out by:

(a) A CAS Working Group on Stratospheric Ozone, whose role is to consider and recommend scientific goals and plans for the project. With the help of additional expertise where necessary, the group provides the Executive Committee and the Secretary-General with advice on details of the objectives of the project and how these could be achieved in principle;

(b) A project co-ordinator, assisted by consultants as necessary, working at the WMO Secretariat, using the available experience and support of the Secretariat and other relevant working groups. He will co-ordinate the implementation of the project in line with guidance given by the CAS working group and the Secretary-General.

13. The WMO Executive Committee should be informed annually of the development of the project and should ensure its implementation to the maximum extent possible. The Secretary-General should arrange for information on the implementation of the project to be made available to Members as well as to UNEP and ICSU.

APPENDIX B

ASSESSMENT OF THE EFFECT OF NITROGEN OXIDES ON OZONE

This appendix gives a short review of the present state of knowledge regarding the effect of nitrogen oxides on stratospheric ozone, including the effect of a number of human activities. The importance of nitrogen oxides for stratospheric ozone follows from the fact that NO and NO_2 destroy ozone via the set of reactions

$$(NO + O_3 \longrightarrow NO_2 + O_2) + (NO_2 + O \longrightarrow NO + O_2) + (O_3 + h\nu \longrightarrow O + O_2) =$$
$$(2\ O_3 \longrightarrow 3\ O_2).$$

Natural sources and sinks of NO and NO_2 in the stratosphere

(a) Oxidation of N_2O

The reaction

$$N_2O + O\ (^1D) \longrightarrow 2\ NO \qquad (1)$$

is now considered to be the main source of nitrogen oxides in the stratosphere, but estimates of the yearly global production of NO following from this reaction varies from approximately 2×10^{33} to 2×10^{34} molecules. The difference between these estimates can be explained mainly by different assumptions regarding the vertical diffusion of N_2O in the stratosphere. Besides reaction (1) there are other processes leading to the loss of N_2O, namely

$$N_2O + O\ (^1D) \longrightarrow N_2 + O_2 \qquad (2)$$

and especially

$$N_2O + h\nu \longrightarrow N_2 + O\ (^1D) \qquad (3)$$

Electronically excited $O\ (^1D)$ atoms are produced in the stratosphere mainly be the photolysis of O_3

$$O_3 + h\nu \longrightarrow O\ (^1D) + O_2 \quad \lambda \leqslant 310\ nm \qquad (4)$$

Most of the $O\ (^1D)$ atoms are deactivated by collisions with O_2 and N_2

$$O\ (^1D) + (N_2,\ O_2) \longrightarrow O\ (^3P) + (N_2,\ O_2) \qquad (5)$$

Besides different assumptions about the diffusion of N_2O in the stratosphere, the above-mentioned difference in global NO production rates can be explained by different assumptions regarding the quantum yields of $O\ (^1D)$ production in reaction (4), the deactivation rate coefficient of $O\ (^1D)$, and the photolysis rates of N_2O, especially the contribution from solar radiation below 200 nm penetrating in the Schumann-Runge band of molecular oxygen.

Recent developments have shown that further revisions of the estimates of NO production rates are necessary because of temperature dependence of the $O(^1D)$ production quantum yield in reaction (4), and of the reaction rates of reactions (1), (2) and (5). Furthermore, there is considerable doubt about the quality of the N_2O absorption cross-section at wavelengths larger than about 250 nm.

(b) Galactic cosmic rays

A continuous flow of energetic protons reaches the Earth mainly at high geomagnetic latitudes ($> 60^o$). These protons cause ionization and production of NO mainly in the lower stratosphere. There is an interesting variation in the production of nitric oxide following solar activity with a period of about 11 years. The estimated global, yearly production of NO varies between about 1.2×10^{33} (at solar maximum) and 1.8×10^{33} molecules (at solar minimum). It appears that these estimates of the production of NO due to the action of galactic cosmic rays is rather well known. It has been proposed that the afore-mentioned solar-cycle variations in NO production would be the cause of variations in total ozone, which have been remarkably large at middle- and high-latitude stations (e.g. ± 5% at Tromsö, 70°N and ± 2% at Arosa, 45°N). Recent, independent, detailed calculations with two-dimensional models (Brasseur and Crutzen) cast considerable doubt on the proposed link between variable input of NO over the solar cycle and the observed variations in total ozone. A search for a different mechanism seems to be justified.

(c) Solar proton events

Sporadic bombardment of the Earth's upper atmosphere at high geomagnetic latitudes ($\Phi > 60^o$) by energetic solar particles (mainly protons) produce large amounts of NO in the same way as galactic cosmic rays. The average energy of solar protons being lower than that of galactic cosmic rays, the production of NO from solar protons occurs generally above 30 km. A recent analysis of three solar proton events gave the following approximate global productions of NO in the stratosphere: 2×10^{33} (Nov. 1960), 6×10^{32} (Sept. 1966), 6×10^{33} (Aug. 1972). According to these calculations the amount of NO formed in the stratosphere during these three solar proton events was comparable to, or larger than, the total annual production of NO from the action of galactic cosmic rays and its variations over the solar cycle.

The solar proton event of August 1972 especially constituted a major perturbation in the chemical conditions in the stratosphere and studies of stratospheric ozone and temperature records are very important to increase our knowledge on the response of the stratosphere to major disturbances and provide a means for validating and improving model simulation of the stratosphere.

(d) Other possible sources for stratospheric NO

Large quantities of NO are produced above 100 km due to the action of short-wave ultraviolet radiation in auroral activity. Fortunately, most of the high altitude NO does not reach the lower portions of the atmosphere due to the photodissociation process

$$NO + h\nu \longrightarrow N + O \quad \lambda \leqslant 192 \text{ nm} \qquad (6)$$

followed by the reaction

$$N + NO \longrightarrow N_2 + O \qquad (7)$$

However, there is the possibility of some leakage of upper-level NO in the winter hemisphere and this possible source of stratospheric NO should be investigated.

Nitric oxide may be produced in the troposphere by biological processes by lightning and by conversion of some NH_3 to NO by gas phase reactions. Little is known of the NO_x budget of the troposphere and it may well be that most NO_x in the troposphere is of industrial origin. It is normally assumed that transport of tropospheric NO_x to the stratosphere is not possible due to the efficiency of rainout and washout processes in the troposphere. Although this is very likely the case for sunlight conditions during which there is a conversion from NO_2 to very soluble and reactive HNO_3 by the reactions

$$NO_2 + OH\ (+M) \longrightarrow HNO_3\ (+M) \qquad (8)$$

there is some doubt whether removal of NO_x is efficient enough during winter conditions to prevent significant transfer of NO_x from ground level to the stratosphere. This is an area of research which deserves particular attention.

Anthropogenic sources of NO in the stratosphere

A number of human activities may lead to increases in the stratospheric NO content and may consequently lower the atmospheric ozone abundance. Among these activities should be mentioned especially:

- changes in the conditions of the soil;
- increased industrial injection of NO at ground level;
- injections of NO_x in the lower stratosphere by stratosphere-flying aircraft (both subsonic and supersonic).

Special attention should be given to the possibility that human activities may cause an increase in the input of N_2O into the atmosphere by intensified agricultural activity and by affecting the physical and chemical conditions of the soil (especially by increasing soil acidity). This important issue is taken up in some detail in paragraph 29 of this report.

Nothing quantitative can be said presently of the possible size of the input of industrial ground-level NO_x into the stratosphere and it remains to be seen whether this may in fact constitute a significant problem.

Some consequences of stratospheric flights

Extensive research activities have recently been devoted to the assessment of the impact of stratosphere-flying aircraft on the ozone layer. Research documents and conclusions have been published in the U.S.A., and recently results have become available from programmes in some other countries.

The principal results of the CIAP Report of Findings are summarized in Table Table 1, those of the US National Academy of Sciences report on Environmental Impact of Stratospheric Flight in Table 2, and both of these tables refer to the Northern Hemisphere where the major stratospheric operations are likely to take place. They

TABLE 1: Estimated percent ozone reduction per 100 aircraft

Aircraft type	Fuel burned per year* (kg/yr)	Altitude km (kft)	NO_x Emission Index (EI) Without controls (g per kg fuel)	Percent ozone reduction in Northern Hemisphere		
				Without controls	EI controls	
					1/6 Today	1/60 Today
Subsonic**						
707/DC-8	1×10^9	11 (36)	6	0.0034	0.00070	0.000070
DC-10/L-1011	1.5×10^9	11 (36)	15	0.010	0.0020	0.00020
747	2.1×10^9	11 (36)	15	0.014	0.0025	0.00025
747 — SP	2.0×10^9	13.5 (44)	15	0.079	0.014	0.0014
Supersonic						
Concorde/TU-144	4×10^8 3×10^9	13.5 (44) 16.5 (54)	18	0.39	0.068	0.0068
Advanced SST	3×10^8 6×10^9	16.5 (54) 19.5 (64)	18	1.74	0.32	0.032

* Subsonics assumed to operate at high altitude, 5.4 hours per day, 365 days per year. Supersonics assumed to operate at high altitude, 4.4 hours per day, 365 days per year.

** The present subsonic fleet consists of 1,217 707/DC-8s, 232 DC-10/L-1011s, and 232 747s flying at a mean altitude of 11 km (36 kft) and is estimated to cause a 0.1 percent ozone reduction.

TABLE 2: Percentage reduction in stratospheric ozone per hundred aircraft operating in the stratosphere

Aircraft type	Percentage per 100 aircraft	Uncertainty factor
Present subsonic	0.02	10
Projected subsonic	0.2	10
Present supersonic	0.7	3
Formerly projected supersonic	3	2

are separate assessments of virtually the same set of model results, the higher estimates of the ozone reductions in the NAS Report being mainly due to the introduction of different vertical eddy diffusion coefficients into the model results as derived from a later study of Carbon 14 distributions in the stratosphere. The

uncertainties in the results are stated to be twice to one tenth of the given percentage ozone depletions in the CIAP Table 1. The NAS results have been stated to have uncertainties of a factor of two for flights at 20 km, a factor of three at 17 km and as much as ten for flights at lower altitudes.

Whereas a percentage depletion of 0.39 is suggested in the CIAP report (Table 1) and 0.7 in the NAS report (Table 2), COMESA (United Kingdom) estimates on the basis of injection of 10^{11} g of NO_x per year at an altitude of 16-18 km by 100 Concorde/TU-144 aircraft flying 7 hours per day, that the percentage ozone depletion would be only 0.11%. It should be noted that different assumptions as to the injection rate of NO_x were used by CIAP and NAS.

It is clear that according to these reports there may well be significant reductions in the ozone amounts in the stratosphere if large fleets of SSTs are operated at 20 km or above. On the other hand the effect will be smaller for small aircraft fleets operating at lower altitudes and is likely to be insignificant and undetectable for subsonic fleets now flying and the presently planned number of SSTs (given as about 30 in the CIAP report) likely to operate at 17 km (see paragraph 56 of the report).

APPENDIX C

THE CHLOROFLUOROMETHANES AND THE OZONE DEPLETION PROBLEM

Stratospheric chlorine chemistry

The two chlorofluoromethane gases, CF_2Cl_2 (Fluorocarbon-12) and $CFCl_3$ (Fluorocarbon-11), are now being produced at rates of approximately 500,000 and 300,000 tons respectively, in the world, being used almost entirely in technological applications involving eventual release to the Earth's atmosphere. The only important sink known at present for these molecules is mid-stratospheric photolysis by solar ultraviolet radiation in the 190-220 nm band. Such photolysis results in the immediate release of one chlorine atom per molecule, and a second chlorine atom is rapidly released by the reaction of the remaining radical with O_2. The third atom of Cl from CCl_3F is usually released later by the photolysis of the residual CClFO.

The UV radiation which causes chlorofluoromethane photo-dissociation is also absorbed both by molecular O_2 and by O_3 in the Earth's atmosphere, and has been removed from solar radiation which penetrates to the lower atmosphere. However, as the chlorofluoromethane molecules rise into the stratosphere above most of the O_2 and O_3 due to the atmospheric motions, they encounter this short wave-length solar UV radiation and are photodissociated. The median altitude for release of these Cl atoms is about 30 km.

Free chlorine atoms have long been known from laboratory studies to react very rapidly with ozone by reaction (1),

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (1)$$

and ClO is itself very reactive with two stratospheric components, O and NO, by reactions (2) and (3),

$$ClO + O \longrightarrow Cl + O_2 \qquad (2)$$

$$ClO + NO \longrightarrow Cl + NO_2 \qquad (3)$$

since the concentration of O atoms increases rapidly with altitude, the combination of reactions (1) and (2) is most important above 30 km, and together comprise the ClO_x catalytic chains which result in the removal of two equivalents of ozone by (4)

$$O + O_3 \longrightarrow 2\,O_2 \qquad (4)$$

while returning the Cl to its original form for another cycle.

The repetition of cycles (1) + (2) or (1) + (3) is interrupted by the occasional reaction of Cl with CH_4, H_2, or other H-containing substance to form HCl, as in (5). The catalytic chain can then be restarted by attack of OH on HCl, as in (6)

$$Cl + CH_4 \longrightarrow HCl + CH_3 \qquad (5)$$

$$OH + HCl \longrightarrow Cl + H_2O \qquad (6)$$

At any particular altitude in the stratosphere, the photochemical distribution of chlorine among HCl, ClO and Cl can be calculated in equilibrium if (a) the concentrations of the other reactants (O_3, O, NO, CH_4, H_2, OH) are known; and (b) the rate constants of the reactions (1), (2), (3), (5) and (6) are known by laboratory measurements at stratospheric temperatures. Concentrated research effort during the past year has provided both additional stratospheric measurements and evaluated laboratory rate constants, and this partition of chlorine among HCl, ClO, Cl can now be calculated with reasonable accuracy. At all altitudes, HCl is the most abundant species, but ClO reaches the 10-30% range between 25 and 40 km. Chlorine atoms are always present in lower concentration because of the rapidity of their reaction with ozone.

The current experimental evidence in the stratosphere indicated that this description is essentially correct, and suggests that no undiscovered additional stratospheric chlorine chemistry will materially alter the overall description. A few high altitude samples taken by balloon and analysed in ground laboratories have shown that the mixing ratio of $CFCl_3$ decreases rapidly with altitude above 15 km and is essentially absent above 35 km, as expected on photochemical grounds. CF_2Cl_2 rises higher in the stratosphere because of its lesser photochemical sensitivity, but also has been observed to decrease with altitude. These measurements confirm that both molecules are being decomposed in the mid-stratosphere.

Airborne filters carried into the stratosphere either by aircraft or balloon have been analyzed after return for chlorine content. Neutral filters do not retain any appreciable chlorine when used below 25 km, although they are quite efficient in retaining the particles of sulfuric acid found throughout the lower stratosphere. When coated with a chemical base, however, these filters do retain chlorine in the form of chloride (HCl). The analyses have shown that the amount of chloride retained increases with altitude to about 25-30 km, and agrees with the amounts expected from stratospheric decomposition of $CFCl_3$, CF_2Cl_2, CCl_4, and CH_3Cl. Although the present agreement is much closer, the combined accuracies of the various measurements indicate only that the amount of HCl is within a factor of 2 of that expected. The observed increase of HCl mixing ratio with altitude is inconsistent with tropospheric injection of chloride, either as NaCl from sea salt or as HCl from industrial sources or volcanoes, but is consistent with mid-stratospheric release of chlorine atoms from these organo-chlorine molecules. Since HCl, ClO and Cl are all interconnected by the chemical reactions given above, any unknown reaction of Cl or ClO would also reduce the concentration of HCl. Further verification that HCl is present in approximately the amounts expected would indicate that the major chlorine reactions have probably been included.

Direct measurements of Cl in the stratosphere will be very difficult because of its low concentrations. Direct measurement of ClO has not been made (although instruments for this purpose are being constructed and tested) so that it has not yet been possible to obtain further confirmation in this way. The neutral filter measurements of chloride have, however, consistently shown positive measurements above 25 km, indicating the presence of a new chlorine species. The amounts are consistent with those expected for ClO, but laboratory tests are needed to identify the species involved.

Ozone depletion of ClO_x

The relative rates of removal of ozone can be estimated from direct stratospheric measurements of the concentrations of the important species. In the natural atmosphere, the dominant process involves the NO_x-catalyzed chain, proceeding largely through reactions such as (7)

$$NO_2 + O \longrightarrow NO + O_2 \qquad (7)$$

Lesser amounts of ozone are also removed by the direct reaction of O with O_3 as in (4), and the various HO_x-catalyzed chains. A minor contribution is also made by ClO_x-catalyzed chains of natural origin (e.g. Cl from CH_3Cl).

The present contributions to ozone removal from anthropogenic ClO_x are small, but that part caused by CF_2Cl_2 and CF_3Cl can be expected to increase with time because of the long lifetime of these molecules in the atmosphere. The lifetime for $CFCl_3$ for a stratospheric photochemical sink has been calculated using one-dimensional models to be about 50-70 years, and comparison of actual atmospheric concentrations with known world production indicates an observed lifetime of more than 30 years, with no other appreciable sinks yet discovered. With continued release to the atmosphere it can be expected that the concentrations of both CF_2Cl_2 and $CFCl_3$ will increase, the amounts of ClO in the stratosphere will increase correspondingly, and the amounts of ozone removed by reactions (1) + (2) will then also increase. At present rates of world use, the amounts can be expected to increase to at least 10 times the present concentrations. Accelerated use (world use of $CFCl_3$ and CF_2Cl_2 has increased by about 13% per year from the 1950s to 1973) would result in even higher concentrations. At these higher concentrations, direct comparison of removal rates of O by reaction with NO_2, O_3, and ClO (as in (7), (4) and (2)) indicate that anthropogenic ClO would be an important additional process for removal of ozone, and the average amount of ozone in the Earth's atmosphere would be appreciably decreased.

Several quantitative evaluations, based on calculations using one-dimensional models with transport represented by vertical eddy diffusion, have now been made of progressive effects of anthropogenic ClO_x on the average amount of ozone. These calculations involve average concentrations of the important atmospheric species (taken from the limited observations so far available) and the best current estimations of reaction rates (as measured in laboratories) for about one hundred chemical reactions. On an average world-wide basis, without allowance for variations with latitude and longitude, the calculations indicate that the present anthropogenic depletion of ozone by CF_2Cl_2 and $CFCl_3$ is in the range of 0.5 to 2.0 per cent, and the long-term steady-state effect of continued release at the 1972 world rate of production would be about 10% average ozone depletion with the factor of uncertainty of about two. Preliminary calculations, using models which include latitude variations, indicate ozone depletion of about the same value.

Thus whilst a fuller understanding of the chemistry involving chlorine in the stratosphere will require further measurements and calculations, including the naturally-occurring chlorocarbons (e.g. methyl chloride - CH_3Cl, and possibly others), the present evidence strongly support the view that a continued release of chlorofluormathanes into the atmosphere may lead to a signficant reduction in stratospheric ozone.

Other chlorine compounds

Chlorine atoms can also be released in the stratosphere by reactions of other chlorine-containing molecules such as CCl_4, CH_3Cl, CH_3CCl_3, etc. The atmospheric chemistry of CCl_4 is similar to that of CF_3Cl and CF_2Cl_2, with the solar ultraviolet sink probably of major importance. However, the amount of CCl_4 in technological application involving release to the atmosphere appears currently to be small compared to that of the chlorofluoromethanes.

Chlorocarbon molecules containing C-H bonds also have a major tropospheric sink through reaction (8), illustrated with CH_3Cl, while chlorocarbon molecules

$$OH + CH_3Cl \longrightarrow H_2O + CH_2Cl \qquad (8)$$

containing C = C bonds, e.g. $CCl_2 = CCl_2$, are also removed for the most part by reactions in the troposphere. Nevertheless, a minor fraction of each species will penetrate into the stratosphere and release Cl atoms there. It is therefore important to monitor these additional species continually, and to evaluate the relative importance of tropospheric and stratospheric sinks for each.

The concentration of CH_3Cl in the atmosphere is much too large for the input to be entirely from ordinary industrial sources, and it probably arises chiefly from natural sources. However, the possibility that some of it may be of anthropogenic origin through agricultural practices, e.g. burning of vegetation, requires thorough investigation. Similarly, the anthropogenic and/or natural sources should be determined for the other halocarbons found to be widely distributed in the atmosphere, e.g. CCl_4, $CHCl_3$.

Chlorine nitrate

The chlorine and nitrogen radicals may interact through

$$ClO + NO_2 \longrightarrow ClNO_3 \qquad (9)$$

forming chlorine nitrate. This could be an important reaction from the point of view of ozone photochemistry because it removes radicals from both the chlorine and nitrogen systems, and it is these radicals that may play such a large role in the catalytic destruction of ozone. The above reaction was recognized only recently as being of potential importance in ozone photochemistry, and partly because of it, the NAS report was delayed a few months. On the basis of the above reaction, the NAS reduced the ultimate ozone depletion (assuming continued fluorocarbon release at the 1973 rate) by a factor of 1.85, or from 14% to 7.5%. Recent calculations and observations suggest that the chlorine nitrate concentration in the stratosphere is less than 2 ppb, or considerably less than thought possible a few months ago. This may be because the hydroxyl radicals combine more readily with nitrogen dioxide than does chlorine monoxide, i.e.

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M \qquad (10)$$

is much slower than the reaction

$$OH + NO_2 + M \longrightarrow HNO_3 + M. \qquad (11)$$

This in turn implies that the NAS may have overestimated the factor by which the ozone reduction should be decreased. One recent opinion is that the peak ozone reduction should be more nearly 10% than 7.5%.

APPENDIX D

THE NITROGEN CYCLE

The bulk of the Earth's volatile nitrogen, approximately 4×10^{15} tonnes, resides in the atmosphere as molecular nitrogen (N_2). The remainder, approximately 6×10^{14} tonnes, is distributed between sediments, the ocean, the soil and the biosphere, in concentrations as shown in Table below. The biological processes play a major role in regulating the manner in which nitrogen is exchanged between the various reservoirs.

TABLE: Nitrogen content of various terrestrial reservoirs

Reservoir	Nitrogen content (tonnes)	Reference*
Atmosphere	4×10^{15}	(1)
Land biomass	1×10^{10}	(2)
Humus	6×10^{10}	(3)
Soil inorganic	1×10^{11}	(4)
Ocean biomass	8×10^{8}	(5)
Ocean organic	2×10^{11}	(5)
Ocean Nitrate	6×10^{11}	(6)
Ocean Ammonia & Nitrate	1×10^{10}	(6)
Ocean N_2	2×10^{13}	(6)
Sediments	6×10^{14}	(1)

* (1) H.D. Holland, private communication, 1975.
(2) McElroy, assuming a C to N ratio of 30 (the C to N ratio of trees is typically in the range 20-40).
(3) McElroy, assuming a C to N ratio of 15, (I. Chet, private communication, 1975).
(4) C.C. Delwiche, the Biosphere, W.H. Freeman & Co., San Francisco, 1970.
(5) McElroy, assuming a C to N ratio of 12 (R. Mitchell, private communication, 1975).
(6) R.F. Vaccaro, Chemical Oceanography, Vol.I, Academic Press, London, New York, 1965.

Nitrogen is an essential nutrient and yet in theform in which it may be utilized by the biosphere it is in remarkably limited supply. Before atmospheric nitrogen can be incorporated into the tissue of living things it must be fixed, i.e. it must be transformed from the relatively abundant though chemically inert form of N_2 into more useful compounds such as ammonia (NH_3) and NO_3^-. Such transformation requires a significant input of energy; 226 kilocalories (946 kJ) per mole is needed to break the N-N bond. This is accomplished either as a byproduct of combustion - in automobiles and stationary power sources, or as a result of the application of fertilizers in agriculture. In 1974, combustion accounted for fixation of approximately 4×10^7 tonnes of nitrogen, and about the same amount was produced from nitrogeneous fertilizers. In the same year natural processes, due mainly to symbiotic associations between certain bacteria (Rhizobium) and plants of the family leguminosae, accounted for a total source of fixed nitrogen estimated at 1.8×10^8 tonnes.

Fixation of atmospheric nitrogen must be balanced on a geological time scale by the reverse process, denitrification, through which N is returned to atmosphere in its most stable forms N_2 and N_2O (nitroux oxide). If denitrification did not occur, in about 10^7 years the supply of N_2 would be exhausted. It appears that most of the biospheric nitrogen is returned to the atmosphere as N_2; the global yield of N_2O relative to N_2, according to current estimates, is about 8%. Most of the N_2O released into the atmosphere decomposes harmlessly to form N_2, but a small fraction (about 5%) is decomposed chemically to yield nitric oxide (NO) and it is this source of NO which is believed to represent the major contribution to the stratospheric budget of NO_x. In this way nature, through complex biotic reactions, has the means of exerting a long-term control over ozone, and the biosphere has the capability of influencing the radiation environment at the surface of the planet. Major components of the nitrogen cycle, with estimates for the rates at which the element is transferred between various reservoirs, are illustrated in the figure below.

Man can influence the nitrogen cycle in several ways. He can do so by agriculture; e.g. fixation of nitrogen in chemical fertilizer plants has grown by a factor of 30 over the past 25 years and will grow by at least a factor of 5 over the next 25 years. This could lead to a very significant increase in the rate of global fixation of N by the turn of the century, and the increase may be even greater if recent advances in genetics should permit the development of new crop species capable of symbiotic fixation in the manner which applies now to the legumes. With the increased production of fixed nitrogen, it is to be expected that there would be a corresponding rise in the rate of denitrification, and thus in the formation of N_2O. Since ozone is largely controlled by the N_2O flux into the stratosphere it is clear that a large increase in the rate of production of N_2O would lead to a significant reduction in ozone.

The rise in the amount of N_2O would be even larger if one considers the possible short-term shifts between aerobic and anaerobic processes, and also the possible changes which may take place in the acidity of rain. A decrease in the pH of rain (i.e. an increase in its acidity) may lead to an increase in the production of N_2O relative to N_2. There are indications that various forms of industrial activity, for example the release of sulphur due to burning of fossil fuels and the smelting of metallic sulphides, are already affecting shifts of this nature. This trend must be watched extremely carefully in order to forestall possible harmful effects on the global atmospheric and biospheric environments.

It seems clear that the matters raised here require further attention. They raise problems of enormous complexity, which affect agriculture, soil science, microbiology, public health and oceanography as well as meteorology.

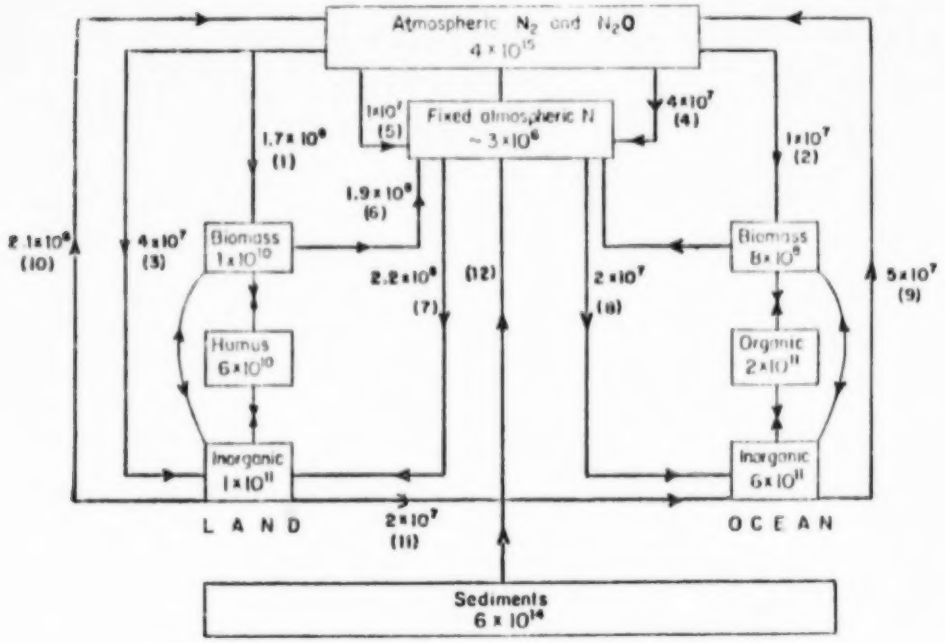

FIGURE: Representation of the nitrogen cycle. Numbers in rectangular boxes give the abundance of N measured in metric tons. Transfer rates are given in tons per year, and the numbers in parentheses define the transfer reactions as follows: (1) land biological fixation, (2) marine biological fixation, (3) fixation in chemical fertilizer, (4) fixation due to combustion, (5) fixation due to lightning, (6) transfer due to volatilization of NH_3, (7) transfer due to rain over land, (8) transfer due to rain over sea, (9) marine denitrification, (10) land denitrification, (11) transfer from land to sea in river run-off, (12) transfer due to raising of sediments, with a comparable amount due to deposition.